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(54) THERMOSENSITIVE COMPOSITION AND ORIGINAL PLATE OF PLANOGRAPHIC PRINTING PLATE USING THE SAME

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a thermosensitive composition capable of causing a high sensitivity irreversible change of physical characteristics when heated and a negative original plate of a planographic printing plate using the composition and capable of high sensitivity recording by a heat mode.

SOLUTION: The thermosensitive composition contains A) a compound which is represented by the formula $R-SO_2-M^+$ (where R is alkyl or aryl and M^+ is a counter cation selected from sulfonium, iodonium, diazonium, ammonium and azinium) and generates a radical under heat, B) a compound whose physical and chemical characteristics undergoes an irreversible change under the radical and, optionally, C) a photothermal conversion agent.

LEGAL STATUS

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to the lithography version original edition which has the recording layer of a large thermosensitive constituent applicable as a thermal recording ingredient, and the negative mold which can be written in by the high sensitivity by the infrared laser using it.

[0002]

[Description of the Prior Art] As for development of the laser in recent years, high power and a miniaturization are progressing with especially **** better **, and the individual laser and the semiconductor laser that have a luminescence field in an infrared field from a near infrared ray. Therefore, such laser is very useful as the exposure light source at the time of engraving directly from digital data, such as a computer. The charge for infrared laser of a negative-mold lithography plate which uses the infrared laser which has a luminescence field in the above-mentioned infrared field as the exposure light source is a charge of a lithography plate which has a recording layer containing a light-and-heat conversion agent, the polymerization initiator which generates a radical with light or heat, and a polymerization nature compound.

[0003] Usually, such an image recording ingredient of a negative mold made the polymerization reaction occur by having made into the initiator the radical generated with light or heat, and uses the recording method which is made to harden the recording layer of the exposure section and forms the image section. In order that such an image formation ingredient of a negative mold may promote the hardening reaction image formation nature is low and according to a polymerization and may form the firm image section as compared with the positive type which makes solubilization of a recording layer cause with the energy of an infrared laser exposure, heat-treating before a development process is common. As an image recording ingredient of the negative mold which performs such afterbaking processing, the record ingredient set to US No. 5,340,699 etc. from the resol resin and novolak resin of a publication is mentioned, for example. When especially an aluminum base material was used, the energy by infrared laser exposure was spread in the thermally conductive high base material, and it was not used for initiation of the polymerization reaction for image formation, and promotion, but there was a problem that sufficient sensibility was not obtained.

[0004]

[Problem(s) to be Solved by the Invention] It is in this invention being made in consideration of the above-mentioned trouble, and the purpose of this invention offering with heating the lithography version original edition of the recordable negative mold by heat mode which an irreversible change of high sensitivity physical properties can be recorded by the thermosensitive constituent which may occur, and the high sensitivity using the constituent, and is unnecessary as for the heat-treatment before development, or can simplify heat-treatment.

[0005]

[Means for Solving the Problem] this invention persons are containing the radical generating agent expressed with the following general formula (I), and the compound from which physical properties'

change with the generated radicals irreversibly wholeheartedly as a result of examination. Header this invention was completed for the ability of high sensitivity-ization of record of the lithography version to be attained by preparing the recording layer which contains a header and still such a constituent for becoming the constituent excellent in the hardenability by heat, and color enhancement. That is, the thermosensitive constituent of this invention is characterized by physical or chemical property containing the compound which changes irreversibly by the compound (a radical generating agent is called suitably hereafter) which generates a radical with the heat expressed with the A following general formula (I), and B radical.

General formula (I) R-SO₂-R expresses an alkyl group or an aryl group among M⁺ type, and M⁺ expresses the opposite cation chosen from sulfonium, iodonium, diazonium, ammonium, and horse mackerel NIUMU. By containing C light-and-heat conversion agent further, the radical of the compound which generates a radical with the heat expressed with A general formula (I) by exposure of the absorption wavelength of C light-and-heat conversion agent occurs in this constituent, and it becomes it recordable [according to / chemical property changes and / exposure] physically physically [of the compound from which chemical property changes irreversibly] by B radical. Moreover, record by heat mode exposure is possible for the lithography version original edition of this invention concerning claim 3, and it is characterized by coming to prepare the radical polymerization initiator expressed with the A following general formula (I), C light-and-heat conversion agent, the compound which has the partial saturation radical of B-1 polymerization nature, and the recording layer containing D binder polymer on a base material.

General formula (I) R-SO₂-R expresses an alkyl group or an aryl group among M⁺ type, and M⁺ expresses the opposite cation chosen from sulfonium, iodonium, diazonium, ammonium, and horse mackerel NIUMU.

[0006] In addition, in this invention, "heat mode correspondence" means that record by heat mode exposure is possible. The definition of the heat mode exposure in this invention is explained in full detail. Hans-Joachim Timpe, IS&Ts NIP 15:1999 International Conference on Digital Printing It is known that carry out optical pumping of the light absorption matter (for example, coloring matter) in a photo conductor ingredient, chemically chemically from optical pumping of the light absorption matter which forms an image through a physical change roughly divide in the process to a physical change, and the two modes exist as indicated by Technologies.P.209. The reacting matter of the others [matter / with which optical pumping of one was carried out / light absorption] in sensitive material, and a certain photochemistry-interaction It is in so-called photon mode which needs for above-mentioned image formation the reacting matter which deactivated by carrying out for example, (energy transfer and an electronic transition), and was activated as the result and which causes chemical or a physical change. The light absorption matter by which optical pumping was carried out generates heat, and deactivates, and another is in so-called heat mode which needs reacting matter for above-mentioned image formation and which causes chemical or a physical change using the heat. In addition, although the special modes, such as multiple photon absorption which absorbs many photons at once, also have the ablation and one molecule which scatter explosively with the luminous energy for which matter gathered locally, it omits here.

[0007] The exposure process using each above-mentioned mode is called font mode exposure and heat mode exposure. The technical difference between font mode exposure and heat mode exposure is whether to be able to use it, being able to add the amount of energy of some photons exposed to the amount of energy of the reaction made into the purpose. For example, it considers causing a certain reaction using n photons. In font mode exposure, since the photochemistry-interaction is used, it cannot be used, being unable to add energy of one photon by the energy of a quantum, and the request of a law of conservation of momentum, and combining. That is, in order to cause a certain reaction, the relation of "the 1 Amount of energy of the amount of energy \geq reaction of a photon" is required. On the other hand, in heat mode exposure, heat is generated after optical pumping, and in order to change and use light energy for heat, help **** of the amount of energy becomes possible. Therefore, the relation of "the amount of energy of the amount of energy \geq reaction of n photons" becomes enough [that].

However, constraint by thermal diffusion is received in this amount addition of energy. That is, if the following optical-pumping-deactivation process will happen by the time heat escapes from the exposure part (reacting point) currently observed now by thermal diffusion, and heat occurs, heat will carry out are recording addition certainly, and will lead to the temperature rise of the part. However, when generating of the following heat is slow, heat escapes and is not accumulated. That is, in heat mode exposure, even if it is the same total amount of exposure energy, about the light of the amount of high energies, results differ and short-time one becomes advantageous to are recording of heat by the long case where a time amount exposure is carried out, in the light of the short case where a time amount exposure is carried out, and the amount of low energy.

[0008] Of course, in font mode exposure, although a phenomenon which was alike under the effect of diffusion of a consecutiveness reaction kind may happen, fundamentally, such a thing does not happen. That is, although it becomes fixed [the proper sensibility (the amount of energy for a reaction required for image formation) of sensitive material] to exposure power density (w/cm^2) (= energy density per unit time amount) in font mode when it sees as a property of sensitive material, the proper sensibility of sensitive material will rise to exposure power density in heat mode. Therefore, in font mode exposure, when the exposure time of extent which can maintain practically required productivity was fixed as an image recording ingredient and each mode is actually compared, although about two about 0.1 mJ/cm high sensitivity-ization can usually be attained, since a reaction occurs with any small light exposure, it is easy to produce the problem of low exposure fogging in the unexposed section. On the other hand, although a reaction does not occur and about two 50 mJ/cm is usually needed from relation with the thermal stability of sensitive material if it is not the light exposure more than [which is heat mode exposure] fixed, the problem of low exposure fogging is avoided. And in heat mode exposure, the exposure power density in the printing plate of sensitive material is required for two or more 5000 w/cm as a matter of fact, and two or more 10000 w/cm is preferably needed. However, it is not desirable from problems, such as ablation happening, if two or more $5.0 \times 10^5 \text{ w/cm}$ high-power consistency laser is used, although not stated in detail here, and soiling the light source.

[0009] Although an operation of this invention is not clear, the radical generating agent shown by A general formula (I) contained in the thermosensitive constituent of this invention It is the compound which has a sulfinic acid in a counter anion with onium salt structure. By B radical which contains the sulfonate ($-\text{SO}_3^-$) generally used as a radical polymerization initiator, and mineral salt (PF_6^- , SbF_6^- , BF_6^-) in [both] a constituent compared with the compound which it has in a counter anion Physical or physical-properties change of the compound from which chemical property changes irreversibly can be performed by high sensitivity. Since the reactivity of a sulfinic acid is high as compared with a sulfonic acid and mineral salt, when heat is applied as a factor of this high-sensitivity-izing, it can react efficient with an onium mother nucleus, and it is possible that many radical kinds are generated.

[0010]

[Embodiment of the Invention] Hereafter, this invention is explained to a detail.

[Thermosensitive constituent] The thermosensitive constituent of this invention by B radical with the radical generating agent expressed with A general formula (I) Physical, since chemical property contains ** containing the compound which changes irreversibly, With heat, the radical generating agent expressed with A general formula (I) decomposes, and a radical is generated. By the radical by B radical A physical and physical characteristic or chemical property of compound from which chemical property changes irreversibly changes, and according to radical polymerization hardening reaction, coloring, a decolorization reaction, etc. arise. Moreover, by containing C light-and-heat conversion agent further to this thermosensitive constituent By irradiating the light of the absorption wavelength of this light-and-heat conversion agent, for example, infrared laser etc. C) a light-and-heat conversion agent generates heat, and with the heat of the light of infrared laser itself, or the heat which C light-and-heat conversion agent generated A) The radical generating agent expressed with a general formula (I) decomposes, a radical is generated, and change of the property of physical and the compound from which chemical property changes irreversibly arises by B radical.

[0011] A) The radical generating agent used by compound this invention which generates a radical with

the heat expressed with a general formula (I) is expressed with the following general formula (I).

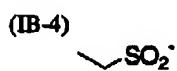
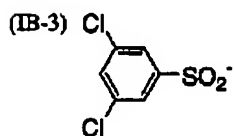
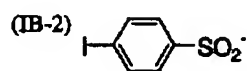
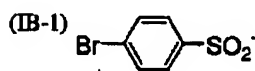
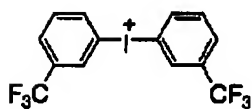
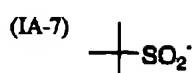
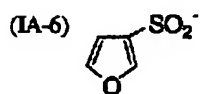
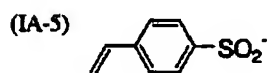
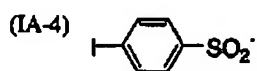
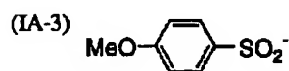
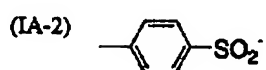
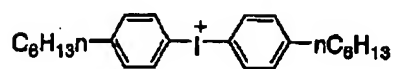
[0012] General formula (I) R-SO₂-R expresses the alkyl group of the carbon atomic numbers 1-20, or the aryl group of the carbon atomic numbers 1-20 preferably among the M⁺ aforementioned type. R may have the ring structure. Moreover, these alkyl groups or an aryl group may have the substituent, as a substituent which can be introduced, an alkyl group, an alkoxy group, an alkenyl radical, an alkynyl group, the amino group, a cyano group, a hydroxyl group, a halogen atom, an amide group, an ester group, a carbonyl group, a carboxyl group, etc. are mentioned, and, specifically, these may have the still more above substituents. Furthermore, two or more substituents join together mutually, and the ring may be formed, and a ring structure may be the heterocycle structure containing a nitrogen atom, a sulfur atom, etc. Especially, from a viewpoint of stability and synthetic fitness, it is desirable that R is an aryl group.

[0013] Moreover, M⁺ expresses the opposite cation chosen from sulfonium, iodonium, diazonium, ammonium, and horse mackerel NIUMU. In the structure, horse mackerel NIUMU has the azine ring which is a six membered ring containing a nitrogen atom, and contains pyridinium, JIAJINIUMU, and thoria JINIUMU here. Horse mackerel NIUMU includes quinolinium, iso quinolinium, benzohorse mackerel NIUMU, naphth horse mackerel NIUMU, etc. including an azine ring and one or more condensed aromatic series rings. What is indicated by USP No. 4,743,528, JP,63-138345,A, 63-142345, 63-142346, and JP,46-42363,B is specifically mentioned, and the opposite cation which forms 1-methoxy-4-phenyl pyridinium tetrafluoroborate and N-alkoxy pyridinium salt is illustrated.

[0014] Also in these opposite cations, the compound which has iodonium or sulfonium as an opposite cation from the field of stability and sensibility is desirable, and the compound which has diaryl iodonium or a triarylsulfonium frame is still more desirable. Although combination with the cation section corresponding to a desirable opposite cation shows the example of a polymerization initiator expressed with a general formula (I) below, this invention is not restricted to this. As desirable structure of an iodonium frame, from the field of stability, a diaryl sulfonium frame is desirable and the aryl group may be permuted like the above-mentioned aryl group. Below, a desirable iodonium salt (let iodonium be opposite cation) compound [an instantiation compound (IA-1) - instantiation compound (IJ-5)] is illustrated first.

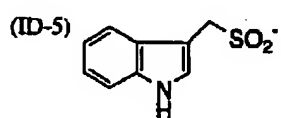
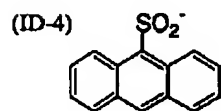
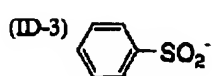
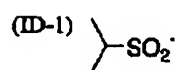
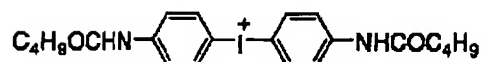
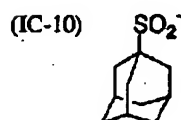
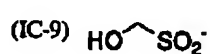
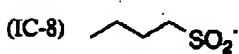
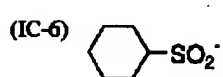
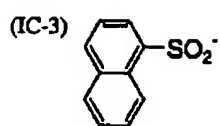
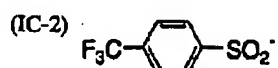
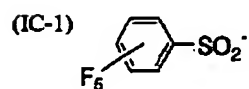
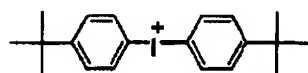
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[Formula 1]



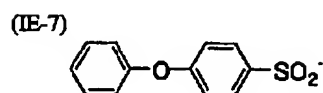
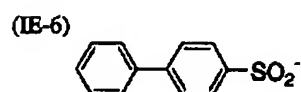
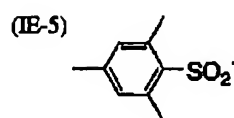
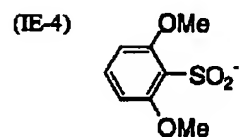
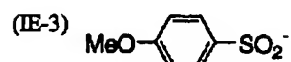
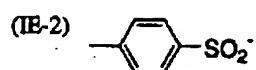
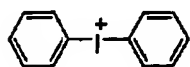
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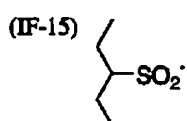
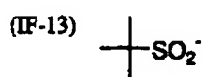
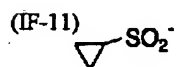
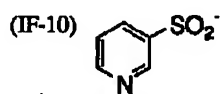
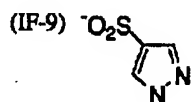
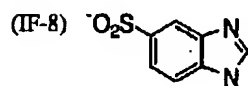
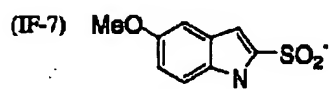
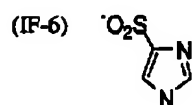
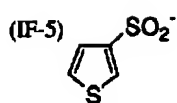
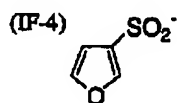
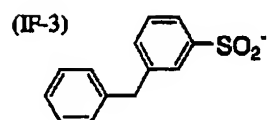
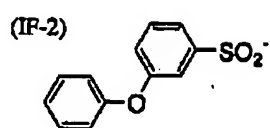
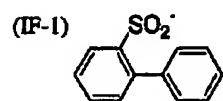
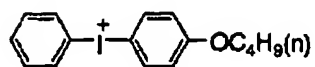
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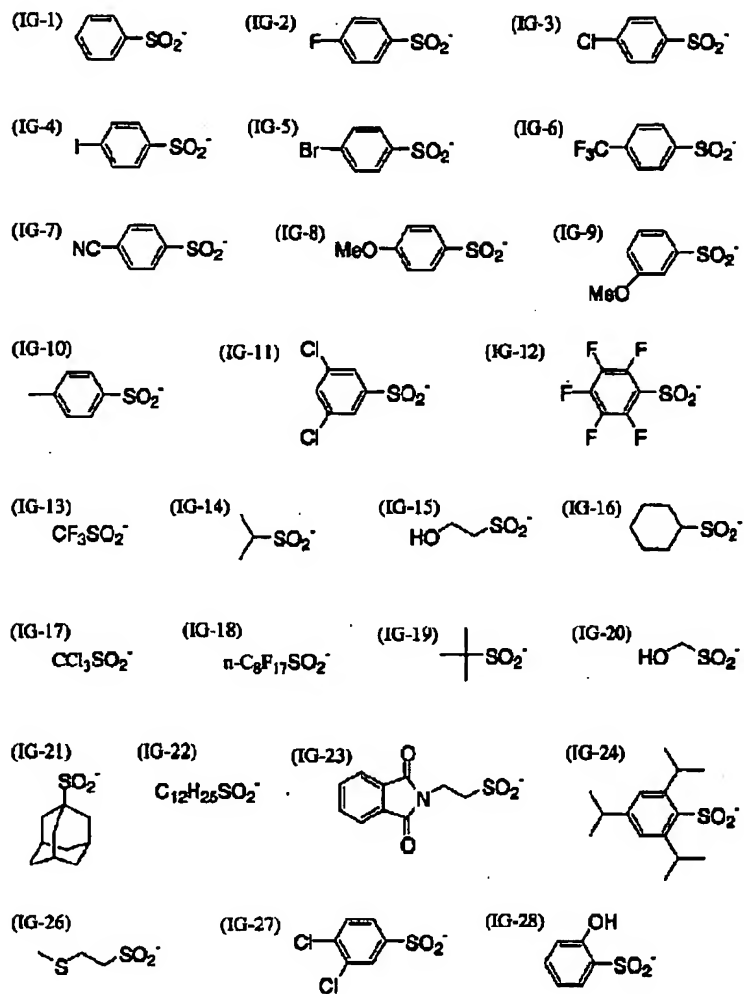
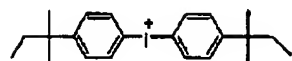
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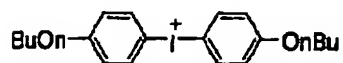


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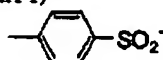
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[0020]
[Formula 6]



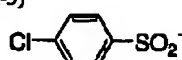
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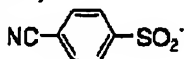
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(IH-3)



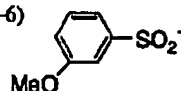
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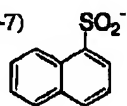
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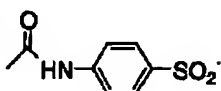
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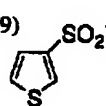
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(IH-8)



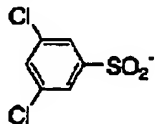
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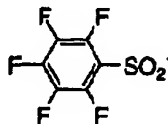
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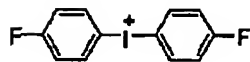
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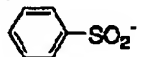
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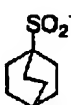
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(U-1)



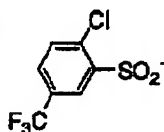
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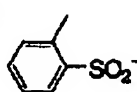
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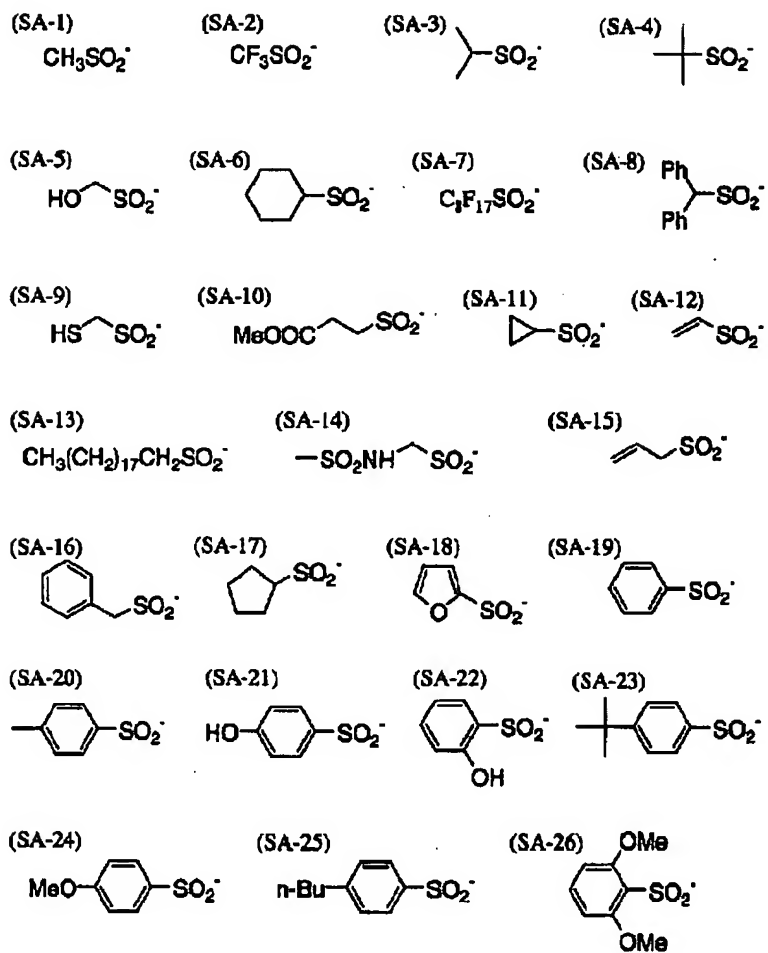
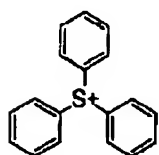
(U-5)



[0021] As desirable structure of a sulfonium frame, from the field of sensibility and stability, a triarylsulfonium frame is desirable and the aryl group may be permuted like the above-mentioned aryl group. Next, a desirable sulfonium salt (let sulfonium be opposite cation) compound [an instantiation compound (SA-1) - instantiation compound (SH-2)] is illustrated.

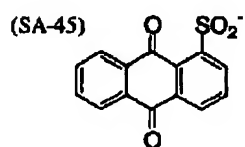
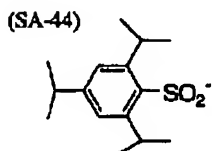
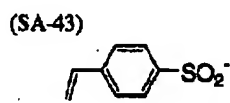
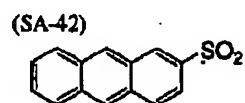
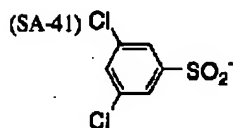
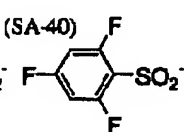
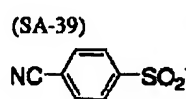
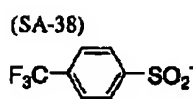
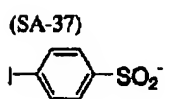
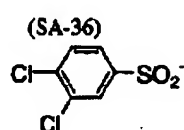
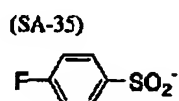
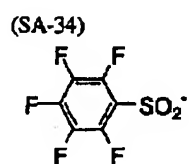
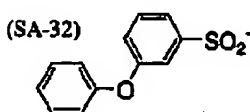
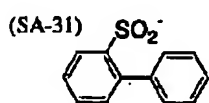
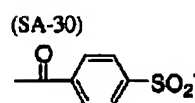
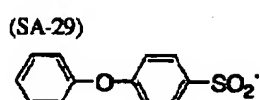
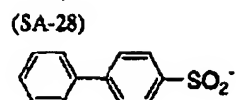
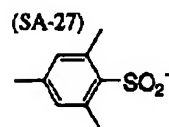
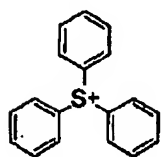
[0022]

[Formula 7]

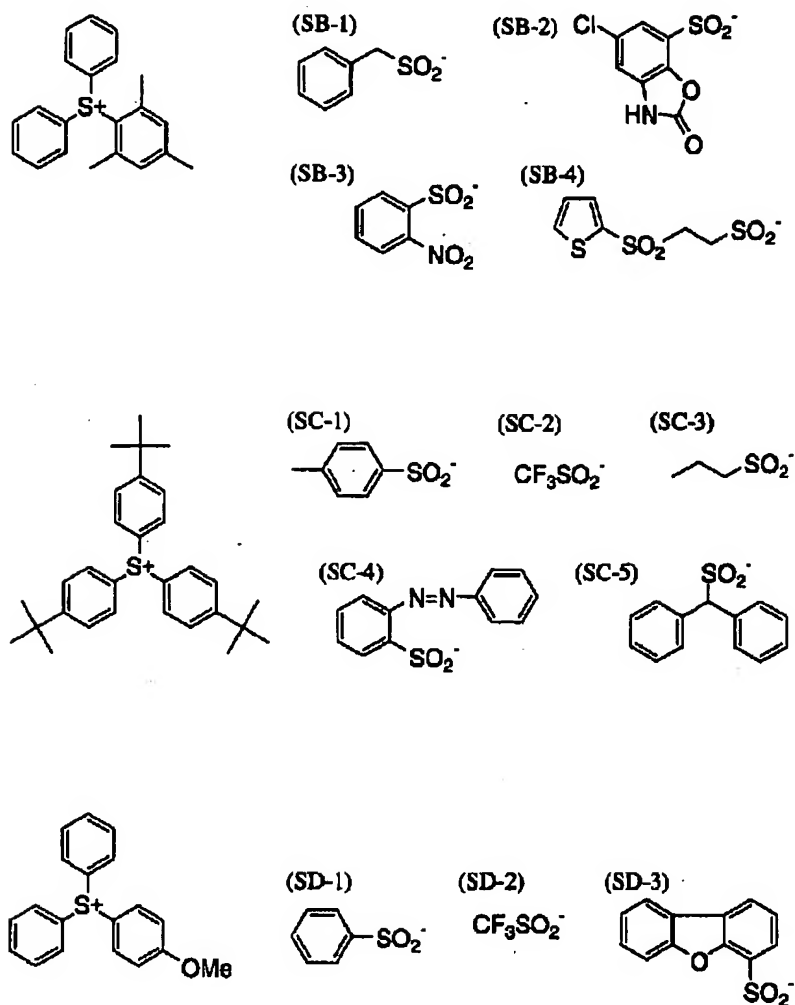


[0023]

[Formula 8]

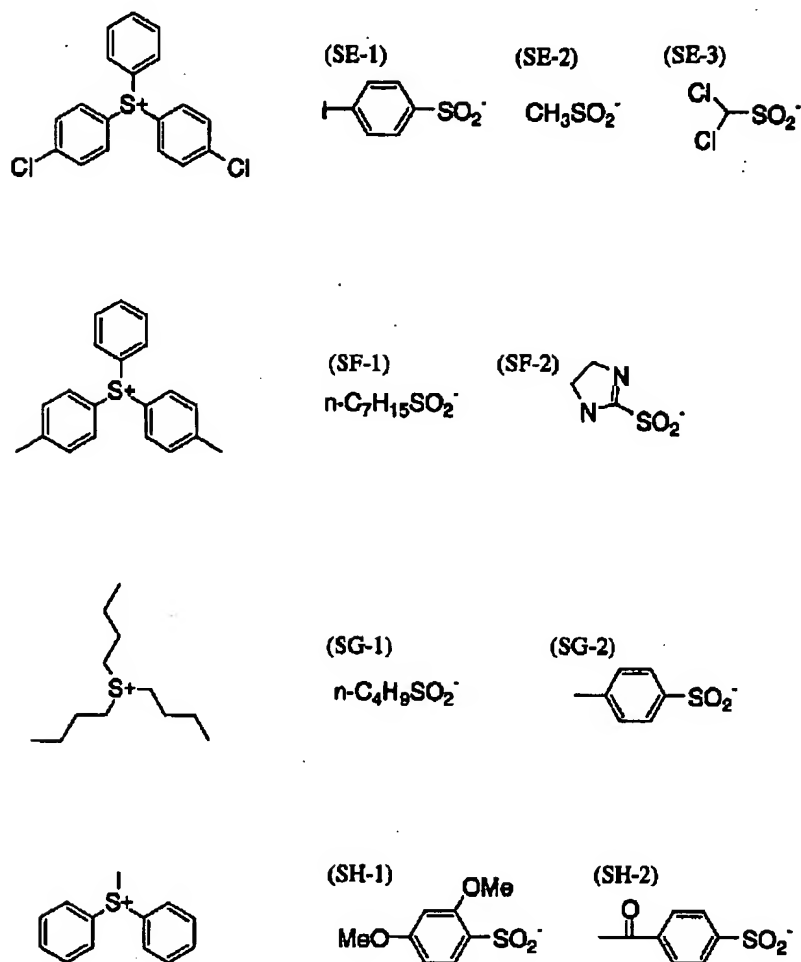


[0024]
[Formula 9]



[0025]

[Formula 10]



[0026] The synthetic example of an instantiation compound (SA-20) is shown as a typical example. Diphenyl sulfoxide 50.9g was dissolved in benzene 800ml, 200g of aluminum chlorides was added to this, and it flowed back for 24 hours. It flowed into water 2L slowly under ice-cooling of reaction mixture, 400ml of concentrated hydrochloric acid was added to this, and it heated at 70 degrees C for 10 minutes. After washing and filtering this water solution by 500ml of ethyl acetate, what dissolved 200g of ammonium iodide in 400ml of water was added. When ethyl acetate **** and after rinsing washed the fine particles which deposited and it dried, 70g of triphenylsulfonium iodide was obtained.

Triphenylsulfonium iodide 7.8g was dissolved in methanol 100ml, 4.98g of silver oxides was added to this solution, and it agitated at the room temperature for 4 hours. The solution was filtered, p-toluene sulfinic-acid sodium of an excessive amount was added to this, and 2ml of concentrated hydrochloric acid was added further. Viscous oil was obtained by condensing reaction mixture, washing concentration liquid by ethyl acetate and the hexane, and performing a vacuum drying. this -- chloroform -- dissolving -- filtering -- concentration -- carrying out -- this process -- 2 times -- repeating -- the shape of viscous oil -- SA-20 were obtained. Starting material and the sulfinic acid to add are compoundable similarly by choosing suitably about other sulfonium salt and iodonium salt.

[0027] As other methods of obtaining iodonium iodide, moreover, Bull.Chem.Soc.Jpn.70,219-224 (1997), Bull.Chem.Soc.Jpn.70, 1665-1669 (1997), The approach of Bull.Chem.Soc.Jpn.70,115-120 (1999), J.Amer.Chem.Soc;82;1960, 725-731, J.Amer.Chem.Soc;81;1959, and 342 -346 publication etc. can be used.

[0028] As other methods of obtaining sulfonium iodide, the approach of a publication etc. can be used for J.Amer.Chem.Soc;91;1969;145-150.

[0029] As for the radical generating agent expressed with said general formula (I) by the thermosensitive constituent of this invention, it is desirable to contain 0.5 to 20% of the weight among

the total solids which constitute a constituent.

[0030] In this invention, unless the effectiveness of this invention is spoiled in addition to said specific radical generating agent, other well-known (it does not have sulfinic-acid structure) photopolymerization initiators, a thermal polymerization initiator, etc. can be chosen and used together. As a polymerization initiator in which these concomitant use is possible, the well-known onium salt which does not have sulfinic-acid structure, the triazine compound which has a trihalomethyl group, a peroxide, an azo system polymerization initiator, an azide compound, quinone diazide, etc. are mentioned to the section for a cation, for example.

[0031] As an example of the onium salt which can be suitably used as a radical generating agent which can be used together, what was indicated by paragraph number [of a Japanese-Patent-Application-No. No. 310623 / 11 to / specification] [0030] - [0033] can be mentioned.

[0032] Moreover, well-known polymerization initiators, such as a thermal polymerization initiator of a publication, are also preferably used for the paragraph number [0016] of an onium salt and a JP,8-108621,A official report expressed with the general formula (I) of a publication - (IV) to paragraph number [of JP,9-34110,A] [0012] - [0050]. When using other polymerization initiators together, as for these contents, it is desirable to carry out to said 50 or less % of the weight of specific radical generating agent. As for the radical generating agent used in this invention, it is desirable that absorption maximum wavelength is 400nm or less, and it is desirable that it is 360 morenm or less. Thus, the handling [an image formation ingredient] under a white light by making absorption wavelength into an ultraviolet-rays field.

[0033] B) Chemical property states physical and the compound which changes irreversibly with a radical by physical and B radical whose chemical property is the 2nd indispensable component in the thermosensitive constituent of compound this invention which changes irreversibly. According to an operation of the radical generated with the heat of said radical generating agent, that physical characteristic or chemical property changes, especially if this compound is a compound with which that condition of having changed is held and is a compound which has such a property, it does not have a limit and the compound of arbitration can be used for it. For example, many compound itself mentioned in said A radical generating agent has such a property. As a property of the changing compound of B by the radical generated from the radical generating agent, physical properties like an ingredient, such as physical properties like a molecule, such as an absorption spectrum (color), the chemical structure, and polarizability, solubility, reinforcement, a refractive index, a fluidity, and adhesiveness, are mentioned, for example.

[0034] When the compound from which an absorption spectrum changes with oxidization and reduction, or **** addition reactions is used as a compound of B), oxidization by the radical generated from a radical generating agent, reduction, etc. are caused, and image formation is possible. Such an example is indicated by J.Am.Chem.Soc., 108,128 (1986), J.Imaging.Soc., 30,215 (1986), Israel.J.Chem., and 25,264 (1986).

[0035] Moreover, it is possible as a compound of B to form thermosetting resin or a negative-mold photopolymer by combining with A radical generating agent using the compound in which addition polymerization or condensation polymerization is possible.

[0036] Although the content of the compound of B) chooses the optimal amount suitably with property change made into the purpose, or the compound used, when the compound from which an absorption spectrum changes with oxidation and reduction, or **** addition reactions is generally used for it, it is about 10 - 80 % of the weight among constituent total solids, and when the compound in which addition polymerization or condensation polymerization is possible is used, it is about 10 - 90 % of the weight among constituent total solids. Preferably, it is 20 - 80% of the weight of the range, and is 30 - 70% of the weight of the range still more preferably.

[0037] As a compound of suitable B for manufacture of the high sensitivity lithography version original edition which is one of the purposes of this invention, the compound which has the partial saturation radical of B-1 polymerization nature is mentioned. This compound is explained below at a detail.

B-1) The compound which has the partial saturation radical of the polymerization nature used for

compound this invention which has the partial saturation radical of polymerization nature is an addition polymerization nature compound which has the ethylene nature partial saturation double bond of a piece at least, and is preferably chosen from the compound which has preferably at least one end ethylene nature unsaturated bond two or more **. Such a compound group is widely known in the industrial field concerned, and can use these without limitation especially in this invention. These include a thing with the chemical form of a monomer, a prepolymer, i.e., a dimer, a trimer and oligomer or those mixture, those copolymers, etc. As an example of a monomer and its copolymer, unsaturated carboxylic acid (for example, an acrylic acid, a methacrylic acid, an itaconic acid, a crotonic acid, isocrotonic acid, a maleic acid, etc.), and the ester and amides are raised, and the ester of unsaturated carboxylic acid and an aliphatic series polyhydric-alcohol compound and the amides of unsaturated carboxylic acid and an aliphatic series multiple-valued amine compound are used preferably. Moreover, a dehydration condensation reaction object with the carboxylic acid of the addition reaction object of the unsaturated-carboxylic-acid ester and the amides which have nucleophilicity substituents, such as hydroxyl, and an amino group, a sulfhydryl group, monofunctional or polyfunctional isocyanate, and epoxy, monofunctional, or many organic functions etc. is used suitably.

[0038] Moreover, a substitution reaction object with the alcohols of the unsaturated-carboxylic-acid ester and the amides which have an addition reaction object with the alcohols of the unsaturated-carboxylic-acid ester and the amides which have an isocyanate radical and electrophile nature substituents, such as an epoxy group, monofunctional, or many organic functions, amines, and thiols, a halogen radical, and desorption nature substituents, such as a tosyloxy radical, monofunctional, or many organic functions, amines, and thiols is also suitable. Moreover, it is also possible as another example to use the compound group replaced with partial saturation phosphonic acid, styrene, vinyl ether, etc. instead of the above-mentioned unsaturated carboxylic acid.

[0039] As an example of the monomer of the ester of an aliphatic series polyhydric-alcohol compound and unsaturated carboxylic acid As acrylic ester, ethylene glycol diacrylate, triethylene glycol diacrylate, 1,3-butanediol diacrylate, tetramethylene glycol diacrylate, Propylene glycol diacrylate, neopentyl glycol diacrylate, Trimethylolpropane triacrylate, the TORIMECHI roll pro pantry (acryloyloxypropyl) ether, Trimethylol triacrylate, hexanediol diacrylate, 1, 4-cyclohexane diol diacrylate, tetraethylene glycol diacrylate, Pentaerythritol diacrylate, a pentaerythritol thoria chestnut rate, Pentaerythritol tetra-bitter taste relay **, dipentaerythritol diacrylate, Dipentaerythritol hexaacrylate, a sorbitol thoria chestnut rate, There are sorbitol tetraacrylate, SORUBITO 1 RUPENTA acrylate, sorbitol hexa acrylate, Tori (acryloyloxyethyl) isocyanurate, polyester acrylate oligomer, etc.

[0040] As methacrylic ester, tetramethylene glycol dimethacrylate, Triethylene glycol dimethacrylate, neopentyl glycol dimethacrylate, Trimethylolpropanetrimethacrylate, trimethylolethane trimethacrylate, Ethylene glycol dimethacrylate, 1,3-butanediol dimethacrylate, Hexanedioldimethacrylate, pentaerythritol dimethacrylate, Pentaerythritol trimethacrylate, pentaerythritol tetra-methacrylate, Dipentaerythritol dimethacrylate, dipentaerythritol hexamethacrylate, There are sorbitol trimethacrylate, sorbitol tetra-methacrylate, screw [p-(3-metacryloxy-2-hydroxy propoxy) phenyl] dimethylmethane, screw-[p-(methacrylic oxyethoxy) phenyl] dimethylmethane, etc.

[0041] As itaconic-acid ester, there are ethylene glycol di-itaconate, propylene glycol di-itaconate, 1,3-butanediol di-itaconate, 1,4-butanediol di-itaconate, tetramethylene glycol di-itaconate, pentaerythritol di-itaconate, sorbitol tetra-itaconate, etc.

[0042] As crotonic-acid ester, there are ethylene GURIKORUJI crotonate, tetramethylene glycol JIKUROTNETO, pentaerythritol JIKUROTNETO, sorbitol TETORAJI crotonate, etc. As isocrotonic acid ester, there are ethylene glycol JIISO crotonate, pentaerythritol JIISO crotonate, sorbitol tetrapod iso crotonate, etc.

[0043] As a maleate, there are ethylene glycol JIMARETO, triethylene glycol JIMARETO, pentaerythritol JIMARETO, sorbitol tetra-malate, etc.

[0044] As an example of other ester, JP,46-27926,B, JP,51-47334,B, fatty alcohol system ester given in JP,57-196231,A, JP,59-5240,A, JP,59-5241,A, the thing that has an aromatic series system frame given in JP,2-226149,A, the thing containing the amino group given in JP,1-165613,A, etc. are used suitably.

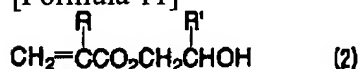
Furthermore, the above-mentioned ester monomer can be used also as mixture.

[0045] Moreover, as an example of the monomer of the amide of an aliphatic series multiple-valued amine compound and unsaturated carboxylic acid, there are methylenebis-acrylamide, methylenebis-methacrylamide, 1, 6-hexa methylenebis-acrylamide, 1, 6-hexa methylenebis-methacrylamide, diethylenetriamine tris acrylamide, xylylene bis-acrylamide, xylylene bis-methacrylamide, etc. As an example of other desirable amide system monomers, a thing with xylene structure can be raised to cyclo given in JP,54-21726,B.

[0046] The urethane system addition polymerization nature compound manufactured using the addition reaction of isocyanate and a hydroxyl group is also suitable. Moreover, as such an example To for example, the poly isocyanate compound which has two or more isocyanate radicals in one molecule indicated in JP,48-41708,B The vinyl urethane compound containing two or more polymerization nature vinyl groups etc. is mentioned into 1 molecule to which the vinyl monomer containing the hydroxyl group shown by the following general formula (2) was made to add.

[0047]

[Formula 11]



[0048] R and R' shows H or CH₃ among a general formula (2). Moreover, urethane acrylate which is indicated by JP,51-37193,A, JP,2-32293,B, and JP,2-16765,B, and the urethane compounds which have JP,58-49860,B, JP,56-17654,B, JP,62-39417,B, and an ethyleneoxide system frame given in JP,62-39418,B are suitable.

[0049] Furthermore, the thermosensitive constituent which was very excellent in the hardening reaction rate depending on using the addition polymerization nature compounds which is indicated by JP,63-277653,A, JP,63-260909,A, and JP,1-105238,A, and which have amino structure and sulfide structure in intramolecular can be obtained.

[0050] As other examples, acrylate and methacrylate of many organic functions, such as JP,48-64183,A, JP,49-43191,B, JP,52-30490,B, polyester acrylate that are indicated by each official report, and epoxy acrylate the epoxy resin and the acrylic acid (meta) were made to react to, can be raised. Moreover, a specific unsaturated compound JP,46-43946,B, JP,1-40337,B, and given in JP,1-40336,B, a vinyl phosphonic acid system compound given in JP,2-25493,A, etc. can be raised. Moreover, in a certain case, the structure containing a perfluoro-alkyl group given in JP,61-22048,A is used suitably. further -- a Japanese adhesion association magazine -- vol.20 and the thing currently introduced to No.7,300-308 page (1984) as a photoresist monomer and oligomer can also be used.

[0051] The detail of operation how whether it is used independently, using what kind of structure or it using together, and an addition are can be set as arbitration in accordance with the engine-performance design of a final sensitized material about these addition polymerization nature compounds. For example, it is chosen from the following viewpoints. In respect of sensitization speed, structure with many partial saturation radical contents per molecule is desirable, and when it is many, two or more organic functions are desirable. Moreover, in order to make high reinforcement of the image section, i.e., the hardening film, the thing of three or more organic functions is good, and the approach of adjusting both for photosensitivity and reinforcement by using together the thing of the different number of organic functions and a different polymerization nature machine (for example, acrylic ester, methacrylic ester, a styrene system compound, a vinyl ether system compound) also has it. [still more effective] While the compound of big molecular weight and a hydrophobic high compound are excellent in sensitization speed and film reinforcement, they may not be preferably in respect of a deposit in development speed or a developer.

[0052] Moreover, also to compatibility with other components in a thermosensitive constituent (for example, a binder polymer, an initiator, a coloring agent, etc.), and dispersibility, selection and the usage of an addition polymerization compound are important factors, for example, may raise compatibility according to use of a low purity compound, and two or more sorts of concomitant use, and it may deal in

it.

[0053] Although characterized by the thermosensitive constituent of this invention discovering the irreversible property change by heat, in addition to the above-mentioned component, by adding a light-and-heat conversion agent, heat mode exposure can be produced, and the above property change can be typically produced with the laser which emits infrared radiation, namely, it can consider as the constituent which has photosensitivity. This C light-and-heat conversion agent is explained below.

C) The light-and-heat conversion agent used for light-and-heat conversion agent this invention absorbs the wavelength of a predetermined light, and has the function changed into heat. Under the present circumstances, the radical generating agent which is the component of A decomposes, and a radical is generated with the generated heat, i.e., heat mode exposure of the wavelength which this C light-and-heat conversion agent may absorb. As a light-and-heat conversion agent, the light energy exposure line used for record is absorbed, and if it is the matter which generates heat, there is especially no limit of an absorption wavelength region, and it can be used. the desirable light-and-heat conversion agent used in this invention -- acquisition -- it is the infrared absorption nature color or pigment which has the absorption maximum in 1200nm from the wavelength of 760nm from a viewpoint of the compatibility to easy high power laser.

[0054] As a color, the well-known thing indicated by reference, such as a commercial color and a "color handbook" (the Society of Synthetic Organic Chemistry, Japan edit, Showa 45 annual publications), can be used. Specifically, colors, such as azo dye, metallic complex azo dye, pyrazolone azo dye, a naphthoquinone color, anthraquinone dye, phthalocyanine dye, a carbonium color, a quinonimine dye, methine dye, cyanine dye, squarylium coloring matter, pyrylium salt, a metal thio rate complex, an oxo-Norian color, a G MONIUMU color, an aminium color, and a crocodile NIUMU color, are mentioned.

[0055] As a desirable color, for example JP,58-125246,A, JP,59-84356,A, The cyanine dye indicated by JP,59-202829,A, JP,60-78787,A, etc., The methine dye indicated by JP,58-173696,A, JP,58-181690,A, JP,58-194595,A, etc., JP,58-112793,A, JP,58-224793,A, JP,59-48187,A, The naphthoquinone color indicated by JP,59-73996,A, JP,60-52940,A, JP,60-63744,A, etc., Cyanine dye the squarylium coloring matter indicated by JP,58-112792,A etc. and given in British JP,434,875,B etc. can be mentioned.

[0056] Moreover, a near-infrared absorption sensitizer given in U.S. Pat. No. 5,156,938 is also used suitably. Moreover, the arylbenzo(thio)pyrylium salt by which the U.S. Pat. No. 3,881,924 publication was permuted, TORIMECHIN thia pyrylium salt given in JP,57-142645,A (U.S. Pat. No. 4,327,169), JP,58-181051,A, 58-220143, 59-41363, 59-84248, 59-84249, 59-146063, The pyrylium system compound indicated by 59-146061, cyanine dye given in JP,59-216146,A, The pyrylium compound currently indicated by the pentamethine thio pyrylium salt of a publication, etc. JP,5-13514,B, and 5-19702 is also preferably used for U.S. Pat. No. 4,283,475.

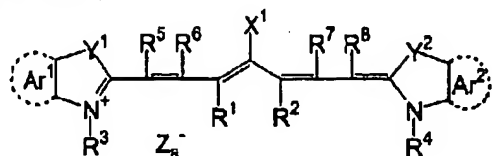
[0057] moreover, the near-infrared absorption color which is indicated by the formula (I) as another example desirable as a color, and is indicated by the U.S. Pat. No. 4,756,993 detail in the letter as (II) can be mentioned.

[0058] As a desirable thing, cyanine dye, phthalocyanine dye, an oxo-Norian color, squarylium coloring matter, pyrylium salt, a thio pyrylium color, and a nickel thio rate complex are especially mentioned among these colors. Furthermore, since the color shown by the following general formula (a) - the general formula (e) is excellent in light-and-heat conversion efficiency, it is desirable, and when it is [polymerization nature / of this invention] under presentation and is used, since the cyanine dye shown especially by the following general formula (a) gives high polymerization activity and is excellent in stability and economical efficiency, it is the most desirable.

[0059]

[Formula 12]

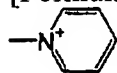
一般式 (a)



[0060] X1 expresses the radical shown in a hydrogen atom, a halogen atom, -NPh₂, X2-L1, or the following among a general formula (a). Here, X2 shows an oxygen atom or a sulfur atom, and L1 shows the hydrocarbon group of the carbon atomic numbers 1-12, the aromatic series ring which has a hetero atom, and the carbon atomic numbers 1-12 containing a hetero atom. In addition, a hetero atom shows N, S, O, a halogen atom, and Se here.

[0061]

[Formula 13]



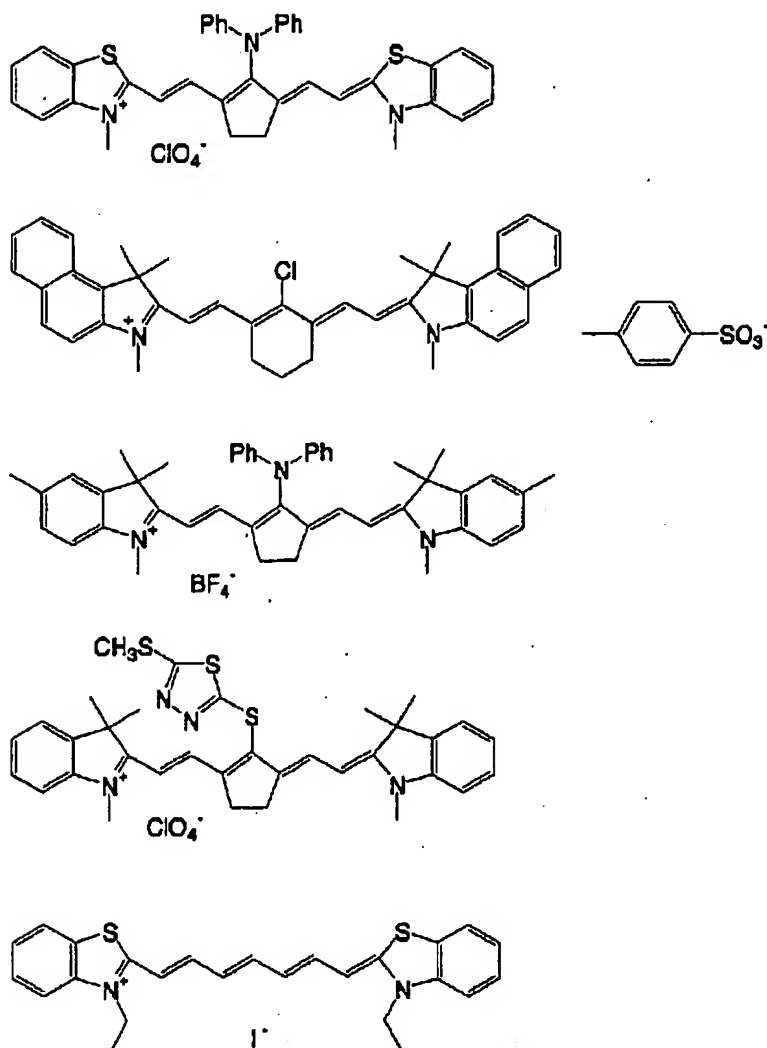
[0062] R1 and R2 show the hydrocarbon group of the carbon atomic numbers 1-12 independently, respectively. Especially the thing for which it is desirable that it is the hydrocarbon group of two or more carbon atomic numbers as for R1 and R2, R1 and R2 are mutually combined further from the preservation stability of recording layer coating liquid, and five membered-rings or six membered-rings are formed is desirable.

[0063] even if Ar1 and Ar2 are the same respectively, they may differ from each other, and they show the aromatic hydrocarbon radical which may have the substituent. The benzene ring and a naphthalene ring are mentioned as a desirable aromatic hydrocarbon radical. Moreover, as a desirable substituent, the alkoxy group of the hydrocarbon group of 12 or less carbon atomic numbers, a halogen atom, and 12 or less carbon atomic numbers is mentioned. even if Y1 and Y2 are the same respectively, they may differ from each other, and they show the dialkyl methylene group of a sulfur atom or 12 or less carbon atomic numbers. even if R3 and R4 are the same respectively, they may differ from each other, and they show the hydrocarbon group of 20 or less carbon atomic numbers which may have the substituent. As a desirable substituent, the alkoxy group of 12 or less carbon atomic numbers, a carboxyl group, and a sulfonic group are mentioned. even if R5, R6, R7, and R8 are the same respectively, they may differ from each other, and they show a hydrogen atom or the hydrocarbon group of 12 or less carbon atomic numbers. From the availability of a raw material, it is a hydrogen atom preferably. Moreover, Z⁻ shows an opposite anion. However, Z⁻ is unnecessary when the sulfonic group is permuted by either R1-R8. Desirable Z⁻ is the halogen ion from preservation stability, the perchloric acid ion, the tetrafluoroborate ion, hexafluorophosphate ion, and sulfonic-acid ion of recording layer coating liquid, and is perchloric acid ion, hexafluoro phosphate ion, and aryl sulfonic-acid ion especially preferably.

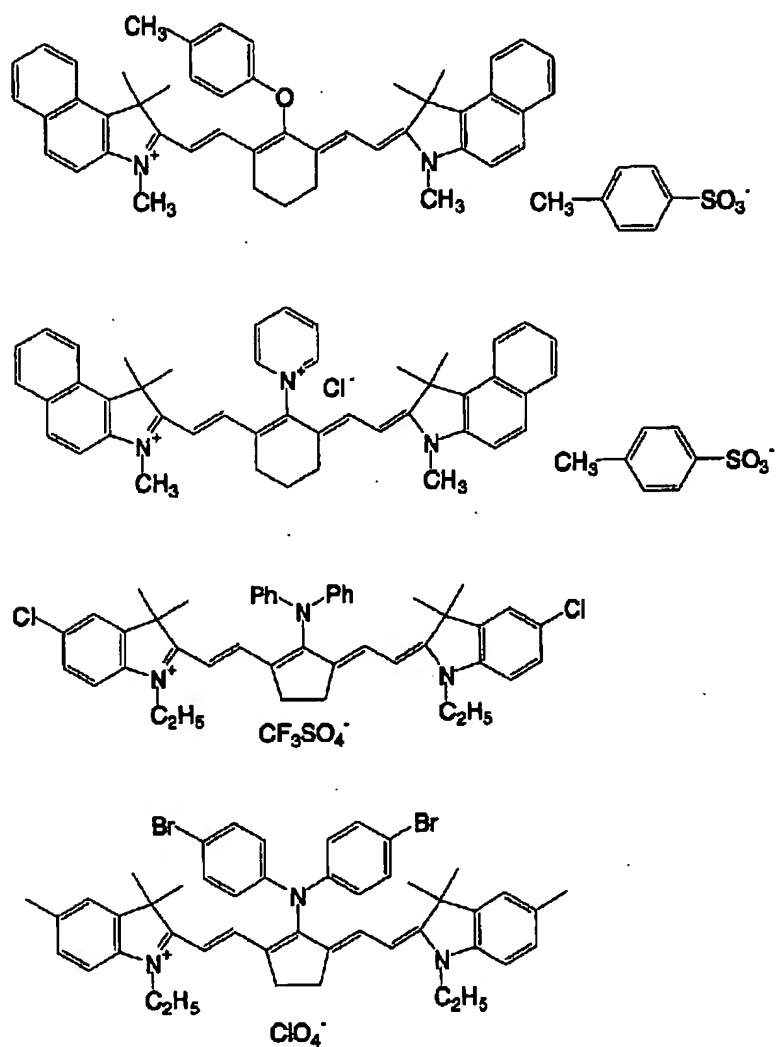
[0064] In this invention, as an example of the cyanine dye shown by the general formula (a) which can be used suitably, although illustrated below, what was indicated by paragraph number [of a paragraph number / of a paragraph number / of an others and Japanese-Patent-Application-No. 11-No. 310623 specification / [0017] - [0019] application-for-patent 2000-No. 224031 specification / [0012] - [0038] application-for-patent 2000-No. 211147 specification] [0012] - [0023] can be mentioned.

[0065]

[Formula 14]

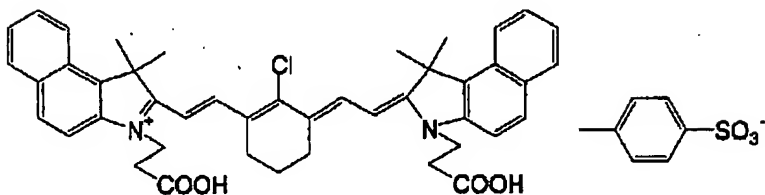
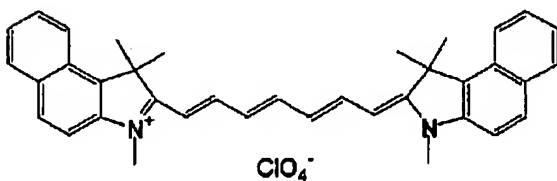
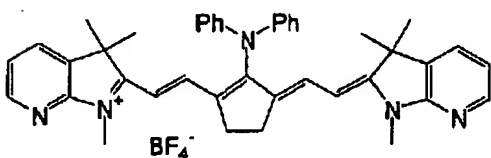
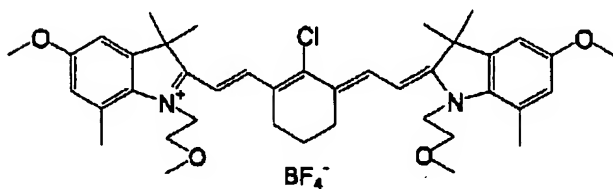
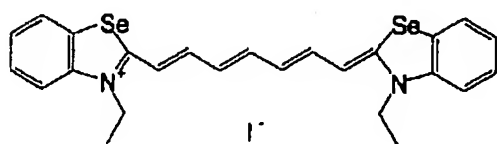


[0066]
[Formula 15]

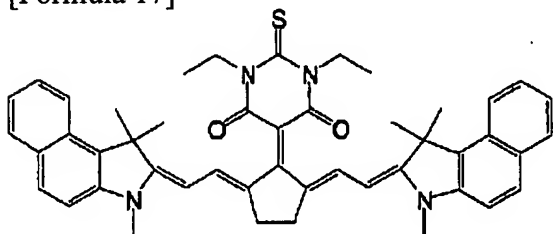


[0067]

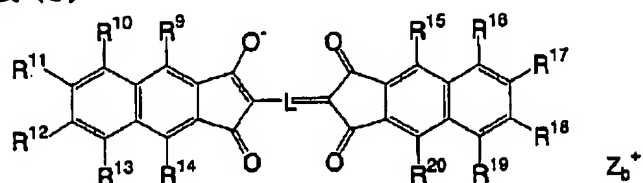
[Formula 16]



[0068]
[Formula 17]



[0069]
[Formula 18]
一般式 (b)

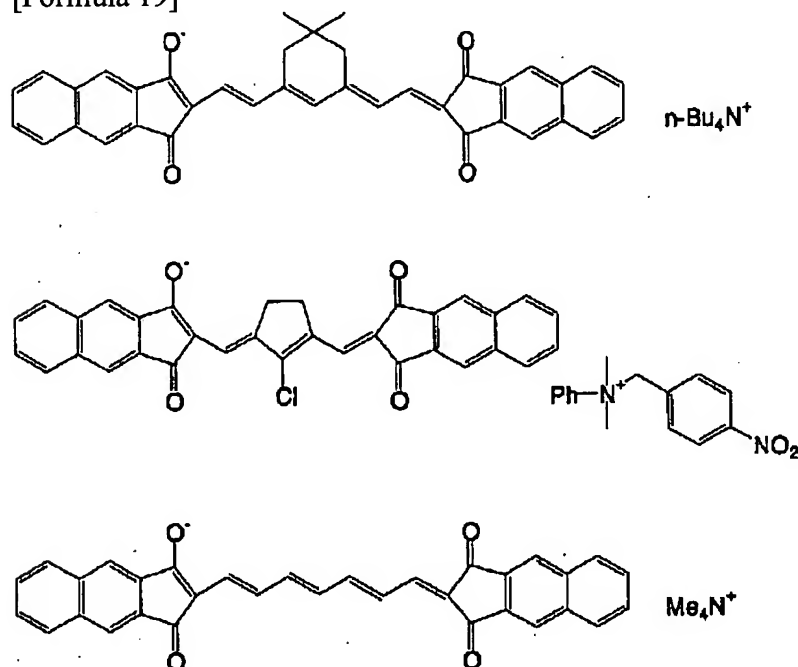


[0070] L may express a seven or more conjugation carbon atomic numbers methine chain among said

general formula (b), this methine chain may have the substituent, and a substituent may join together mutually and it may form the ring structure. Zb^+ shows an opposite cation. As a desirable opposite cation, ammonium, iodonium, sulfonium, phosphonium, pyridinium, an alkali-metal cation (nickel+, K^+ , Li^+), etc. are mentioned. Mutually-independent, R9-R14, and R15-R20 may express two or the substituent combined three, may combine mutually a hydrogen atom or a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl radical, an alkynyl group, a carbonyl group, a thio radical, a sulfonyl group, a sulfinyl group, an oxy-radical, the substituent chosen from the amino group, or these, and they may form the ring structure. Here, what all of the thing to which L expresses the methine chain of the conjugation carbon atomic number 7, R9-R14, and R15-R20 express a hydrogen atom to is desirable from the ease of acquisition, and a viewpoint of effectiveness among said general formula (b). [0071] In this invention, what is illustrated below can be mentioned as an example of the color shown by the general formula (b) which can be used suitably.

[0072]

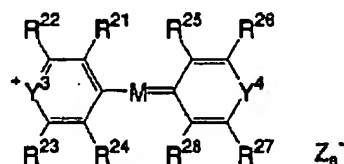
[Formula 19]



[0073]

[Formula 20]

一般式 (c)



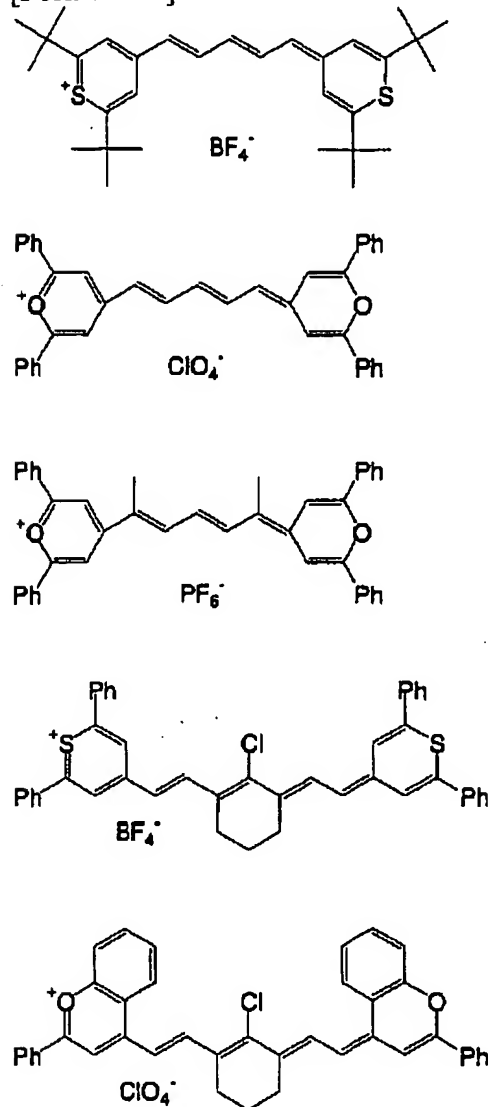
[0074] Y3 and Y4 express an oxygen atom, a sulfur atom, a selenium atom, or a tellurium atom among said general formula (c), respectively. M expresses a with a conjugation carbon numbers of five or more methine chain. Even if R21-R24, and R25-R28 are the same respectively, they may differ from each other, and they express a hydrogen atom, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl radical, an alkynyl group, a carbonyl group, a thio radical, a sulfonyl group, a sulfinyl group, an oxy-radical, or the amino group. Moreover, Zain formula- expresses an opposite anion and is synonymous with Za^- in said general formula (a).

[0075] In this invention, what is illustrated below can be mentioned as an example of the color shown by

the general formula (c) which can be used suitably.

[0076]

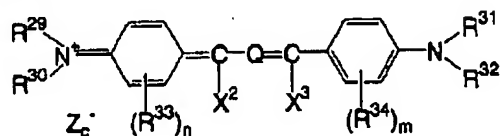
[Formula 21]



[0077]

[Formula 22]

一般式 (d)



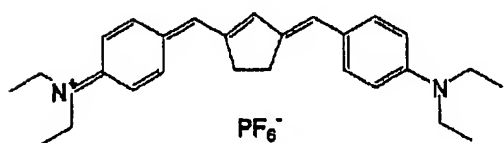
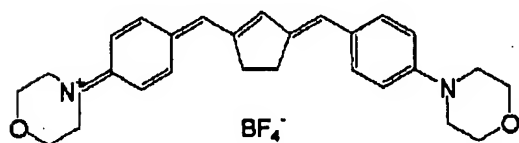
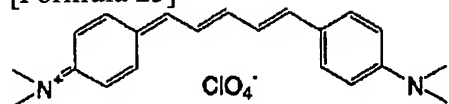
[0078] R^{29} thru/or R^{31} show a hydrogen atom, an alkyl group, or an aryl group independently respectively among said general formula (d). R^{33} and R^{34} show an alkyl group, a permutation oxy-radical, or a halogen atom independently respectively. n and m show the integer of 0 thru/or 4 independently respectively. It may join together and R^{29} , R^{30} , or R^{31} and R^{32} may form a ring, respectively, and R^{29} and/or R^{30} may combine with R^{33} , and R^{31} and/or R^{32} may combine with R^{34} , a ring may be formed, further, when two or more R^{33} or R^{34} exists, it may join together mutually and R^{33} comrades or R^{34} comrades may form a ring. X^2 and X^3 are a hydrogen atom, an alkyl group, or an aryl group independently respectively, and either [at least] X^2 or X^3 show a hydrogen atom or an alkyl

group. Q is the trimethine group or pentamethine radical which may have the substituent, and may form a ring structure with a divalent organic radical. Zc- shows an opposite anion and is synonymous with Za- in said general formula (a).

[0079] In this invention, what is illustrated below can be mentioned as an example of the color shown by the general formula (d) which can be used suitably.

[0080]

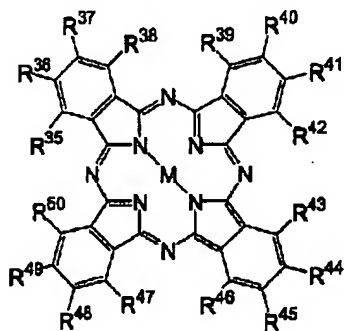
[Formula 23]



[0081]

[Formula 24]

一般式 (e)

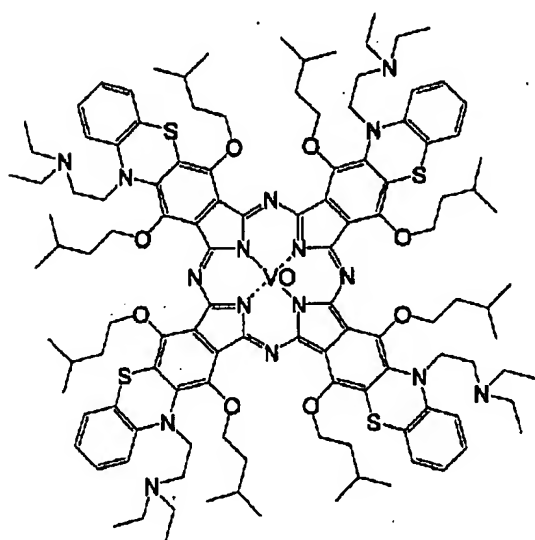
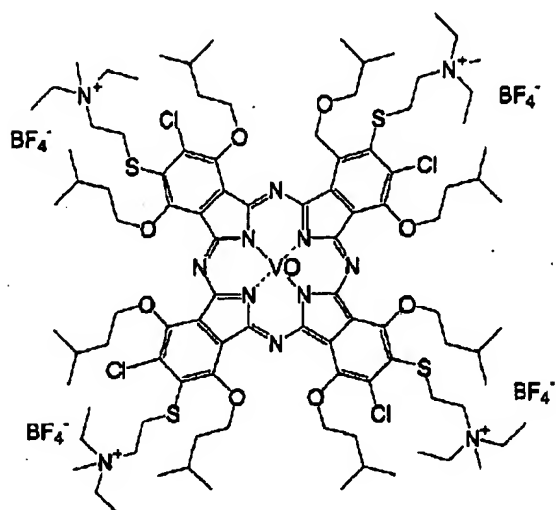


[0082] R35-R50 show independently the hydrogen atom which may have a substituent, a halogen atom, a cyano group, an alkyl group, an aryl group, an alkenyl radical, an alkynyl group, a hydroxyl group, a carbonyl group, a thio radical, a sulfonyl group, a sulfinyl group, an oxy-radical, the amino group, and onium salt structure among said general formula (e), respectively. Although M shows two hydrogen atoms or a metal atom, a halo metal radical, and an oxy-metal radical, as a metal atom contained there, IA of the periodic table, IIA, IIIB, an IVB group atom, and for a start, the transition metals of the second and third period and a lanthanoids are mentioned, and copper, magnesium, iron, zinc, cobalt, aluminum, titanium, and vanadium are desirable [M] especially.

[0083] In this invention, what is illustrated below can be mentioned as an example of the color shown by the general formula (e) which can be used suitably.

[0084]

[Formula 25]



[0085] As a pigment used as a light-and-heat conversion agent in this invention, the pigment indicated by a commercial pigment and a Color Index (C. I.) handbook, the "newest pigment handbook" (volume for Japanese pigment American Institute of Technology, 1977 annual publications), the "newest pigment applied technology" (CMC publication, 1986 annual publications), "printing ink technical" CMC publication, and 1984 annual publications is mentioned.

[0086] As a class of pigment, a black pigment, a yellow pigment, an orange pigment, brown pigments, red pigments, a purple pigment, a blue pigment, green pigments, a fluorescent pigment, a metallic flake pigment, and other polymer joint coloring matter are mentioned. Specifically, insoluble azo pigment, an azo lake pigment, a disazo condensation pigment, a chelate azo pigment, phthalocyanine pigment, an anthraquinone system pigment, perylene and a peri non system pigment, a thioindigo system pigment, the Quinacridone system pigment, a dioxazine system pigment, an isoindolinone system pigment, a kino FUTARON system pigment, a blue-and-white porcelain lake pigment, an azine pigment, a nitroso pigment, a nitro pigment, a natural pigment, a fluorescent pigment, an inorganic pigment, carbon black, etc. can be used. A desirable thing is carbon black among these pigments.

[0087] These pigments may be used without carrying out surface treatment, may perform surface treatment and may be used. In the approach of surface treatment, the approach of carrying out the surface coat of resin or the wax, the approach to which a surfactant is made to adhere, the method of combining the active substance (for example, a silane coupling agent, an epoxy compound, poly isocyanate, etc.) with a pigment front face, etc. can be considered. The above-mentioned surface

treatment approach is indicated by "the property of metallic soap, application" (Saiwai Shobo), the "printing ink technique" (CMC publication, 1984 annual publications), and the "newest pigment applied technology" (CMC publication, 1986 annual publications).

[0088] As for the particle size of a pigment, it is desirable that it is in the range of 0.01 micrometers - 10 micrometers, it is still more desirable that it is in the range which is 0.05 micrometers - 1 micrometer, and it is desirable that it is in the range of 0.1 micrometers - 1 micrometer especially. When the particle size of a pigment is less than 0.01 micrometers, it is not desirable in respect of the stability in the inside of the image recording layer coating liquid of a distributed object, and if 10 micrometers is exceeded, it is not desirable in respect of the homogeneity of an image recording layer.

[0089] As an approach of distributing a pigment, the well-known distributed technique used for ink manufacture, toner manufacture, etc. can be used. As a disperser, an ultrasonic distribution machine, a sand mill, attritor, a pearl mill, a super mill, a ball mill, an impeller, DESUPAZA, KD mill, a colloid mill, a dynatron, 3 roll mills, a pressurized kneader, etc. are mentioned. For details, it is indicated by the "newest pigment applied technology" (CMC publication, 1986 annual publications).

[0090] In this invention, although these light-and-heat conversion agents may use only one sort and two or more sorts can also be used together, the coloring matter shown by the general formula (a) from a viewpoint of sensibility is the most desirable, and the cyanine dye which has a diaryl amino group especially is the most desirable.

[0091] These light-and-heat conversion agents have the desirable thing of total solids added 0.1 to 20% of the weight in a thermosensitive constituent. Since the sensibility of the property change by exposure becomes low in being too fewer than this range, there is an inclination for photosensitivity not to fully be acquired, and it is in the inclination for membranous homogeneity and reinforcement to fall in many [too], neither is desirable.

[0092] The [lithography version original edition] Next, the lithography version original edition of this invention using the aforementioned thermosensitive constituent is explained. Said thermosensitive constituent is used for a recording layer in the lithography version original edition of this invention. (Recording layer) The recording layer which has an image formation function in the lithography version original edition of this invention is explained first. Although the recording layer of the lithography version original edition of this invention contains the radical polymerization initiator expressed with the A following general formula (I), C light-and-heat conversion agent, the compound which has the partial saturation radical of B-1 polymerization nature, and D binder polymer With the heat which C light-and-heat conversion agent generated heat, and the light of infrared laser or C light-and-heat conversion agent generated by the exposure of infrared laser A) The radical generating agent expressed with a general formula (I) decomposes, a radical is generated, the hardening reaction of the compound which has the partial saturation radical of B-1 polymerization nature is promoted, and the image of the negative mold which the exposure section hardens and serves as the image section is formed.

[0093] As for the radical generating agent expressed with said A general formula (I), in forming the recording layer of the lithography version original edition of this invention, it is desirable to contain 0.5 to 20% of the weight among the total solids which constitute a recording layer. This radical generating agent is used combining C light-and-heat conversion agent mentioned later, when it irradiates infrared laser, it generates a radical with that light, heat, or the energy of those both sides, and it has the function which starts the polymerization of the compound which has the partial saturation radical of B-1 polymerization nature, and is promoted.

[0094] What kind of compound although a compound as explanation of the compound of the aforementioned B was explained in full detail is used for the compound which has the partial saturation radical of B-1 polymerization nature used for the recording layer of the original edition for the lithography versions, is used for it can choose specific structure for the purpose which makes adhesion, such as the below-mentioned base material besides the above mentioned requirements, and an overcoat layer, improve. Although more ones are advantageous in sensibility, when the phase separation which is not desirable arises when many [too], or it considers as the problem (for example, the poor manufacture originating in the imprint of a sensitized material component, and adhesion) and the lithography version

original edition on the production process by the adhesiveness of a thermosensitive constituent about the compounding ratio of the B-1 addition-polymerization nature compound in a thermosensitive constituent, problems, like the deposit from a developer arises may be produced. In many cases, from these viewpoints, a desirable compounding ratio is 25 - 75 % of the weight preferably five to 80% of the weight to the constituent total solids which constitute a recording layer. Moreover, these may be used independently or may be used together two or more sorts. In addition, the usage of an addition polymerization nature compound can choose suitable structure, combination, and an addition as arbitration from viewpoints, such as size of the polymerization inhibition to oxygen, resolution, fogging nature, refractive-index change, and surface adhesiveness, and can also enforce an under coat, and the lamination and the method of application which are called finishing further depending on the case.

[0095] in addition, when using said thermosensitive constituent of this invention as a recording layer of the lithography version original edition, into the thermosensitive constituent used for a recording layer, you may add in the same layer as other components, and said C light-and-heat conversion agent carried out can prepare layers other than a recording layer, and can also add them there. When the recording layer (sensible-heat layer) of the negative-mold lithography version original edition is created (film production), it is desirable that the optical density in the absorption maximum in the range of 760nm - 1200nm wavelength of a recording layer is between 0.1-3.0. When it separates from this range, there is an inclination for sensibility to become low. Since optical density is determined by the addition of said C light-and-heat conversion agent, and the thickness of a recording layer, predetermined optical density is obtained by controlling both conditions. The optical density of a recording layer can be measured with a conventional method. As a measuring method, the recording layer of the thickness by which the coverage after desiccation was suitably determined in the range required as a lithography version on transparency or a white base material is formed, a recording layer is formed on the base material of reflexivity, such as the approach of measuring with the optical-density plan of a transparency mold, and aluminum, and the approach of measuring reflection density etc. is mentioned, for example.

[0096] D) In the lithography version original edition of binder this invention of water-insoluble nature and alkali water-solution fusibility, it is desirable to use a binder polymer for a recording layer further. as a binder -- a line -- it is desirable to make an organic macromolecule polymer contain. such -- " -- a line -- anything may be used as organic macromolecule polymer." the line which is the water, weak alkali water solubility, or bloating tendency which enables water development or weak alkaline-water development preferably -- an organic macromolecule polymer is chosen. a line -- according to the application as water, the weak alkaline water, or an organic solvent developer, selection use of the organic macromolecule polymer is carried out only as a coat formation agent of a constituent. For example, water development will be attained if a water-soluble organic macromolecule polymer is used. such a line -- there are what is indicated by the addition polymer which has a carboxylic-acid radical in a side chain, for example, JP,59-44615,A, JP,54-34327,B, JP,58-12577,B, JP,54-25957,B, JP,54-92723,A, JP,59-53836,A, and JP,59-71048,A as an organic giant-molecule polymer, i.e., a methacrylic-acid copolymer, an acrylic-acid copolymer, an itaconic-acid copolymer, a crotonic-acid copolymer, a maleic-acid copolymer, a partial esterification maleic-acid copolymer, etc. Moreover, the acid cellulosic which has a carboxylic-acid radical is in a side chain similarly. In addition, the thing which made the cyclic anhydride add to the addition polymer which has a hydroxyl group is useful.

[0097] In these, according to other addition polymerization nature vinyl monomer] copolymers, and [allyl compound (meta) acrylate / (meta) acrylic acid / need, other addition polymerization nature vinyl monomer] copolymers are excellent in the balance of film reinforcement, sensibility, and development nature [benzyl (meta) acrylate / (meta) acrylic acid / if needed, and it is especially suitable.

[0098] Moreover, very much, since the urethane system binder polymer containing an acid radical indicated by JP,7-12004,B, JP,7-120041,B, JP,7-120042,B, JP,8-12424,B, JP,63-287944,A, JP,63-287947,A, JP,1-271741,A, Japanese Patent Application No. No. 116232 [ten to], etc. is excellent in reinforcement, it is advantageous in respect of print durability and low exposure fitness. Moreover, in accordance with the outstanding development nature and film reinforcement, it has the binder which has an amide group given in JP,11-171907,A, and it is suitable.

[0099] further -- in addition to this -- water solubility -- a line -- a polyvinyl pyrrolidone, polyethylene oxide, etc. are useful as an organic giant molecule. Moreover, in order to raise the reinforcement of a hardening coat, alcoholic fusibility nylon, the polyether of a 2 and 2-screw-(4-hydroxyphenyl)-propane and epichlorohydrin, etc. are useful. these lines -- amounts arbitrary in [all] a constituent can be made to mix with an organic macromolecule polymer However, in exceeding 90 % of the weight, it does not give a desirable result in respect of the image reinforcement formed. It is 30 - 85 % of the weight preferably. moreover, the compound and line which have an ethylene nature partial saturation double bond -- as for an organic macromolecule polymer, it is desirable to consider as the range of 1 / 9 - 7/3 by the weight ratio.

[0100] The binder polymer of this invention is substantially insoluble in water, and a meltable thing is used for an alkali water solution. For this reason, it can restrict to the very small amount used on an environment, not using as a developer the organic solvent which is not desirable. The acid number (what expressed the acid content per polymer lg with the chemistry equivalent number) and molecular weight of such a binder polymer are suitably chosen from a viewpoint of image reinforcement and development nature. The desirable acid number is 0.4 - 3.0 meq/g, the range of desirable molecular weight is 500,000 from 3000, and, for the acid number, the range of 0.6 to 2.0 molecular weight is 10,000 to 300,000 more preferably.

[0101] (E) In the constituent which constitutes the recording layer of the lithography version of other component this inventions, the component of others which were further suitable for the application, the manufacture approach, etc. can be added suitably. Hereafter, it illustrates about a desirable additive. (E-1) By using the additive (it being henceforth called a co-sensitizer) of co-sensitizer *****, sensibility can be raised further. Although these mechanisms of action are not clear, many are considered based on the following chemical processes. That is, a co-sensitizer reacts with various middle active species (a radical, cation) produced in process of the photoreaction started by the thermal polymerization initiator and the addition polymerization reaction which follows it, and what generates a new activity radical is presumed. These react with a radical with low what (a) reduction is carried out and can generate an activity radical greatly, thing which (b) oxidization is carried out and can generate an activity radical, and (C) activity, and there is no accepted theory about whether it changes into a radical with more high activity, or to which [these] although it can classify into what acts as a chain transfer agent, each compound belongs in many cases.

[0102] (a) it has compound carbon-halogen joint association which is returned and generates an activity radical -- carbon-halogen association **** in compound:reduction and it is thought that an activity radical is generated. Specifically, trihalomethyl-s-triazine and trihalomethyl OKISA diazoles can use it suitably.

The compound which has nitrogen-nitrogen association: Nitrogen-nitrogen association **** in reduction and it is thought that an activity radical is generated. Specifically, hexaaryl biimidazole is used suitably.

The compound which has oxygen 1 oxygen association: Oxygen-oxygen association **** in reduction and it is thought that an activity radical is generated. Specifically, organic peroxide is used suitably.

Onium compound: Carbon-hetero association and oxygen-nitrogen association **** in reduction, and it is thought that an activity radical is generated. Specifically, diaryl iodonium salts, triarylsulfonium salts, N-alkoxy pyridinium (horse mackerel NIUMU) salts, etc. are used suitably.

a ferrocene -- an activity radical can be generated in iron arene complex:reduction.

[0103] (b) it oxidizes and an activity radical is generated -- carbon-hetero association **** in compound alkyl ate-complex:oxidization, and it is thought that an activity radical is generated. Specifically, thoria reel alkyl borate is used suitably.

Alkylamine compound: C-X association on the carbon which adjoined nitrogen by oxidization ****, and it is thought that an activity radical is generated. As X, a hydrogen atom, a carboxyl group, a trimethylsilyl radical, benzyl, etc. are suitable. Specifically, ethanolamines, N-phenylglycine, and N-trimethylsilyl methylaniline are raised.

Sulfur-containing yellow, an tin-containing compound: What transposed the nitrogen atom of above-

mentioned amines to the sulfur atom and the tin atom can generate an activity radical according to the same operation. Moreover, the sensitization also according [the compound which has an S-S bond] to S-S **** is known.

[0104] alpha-permutation methyl carbonyl compound: By oxidization, joint **** between carbonyl-alpha carbon can generate an activity radical. Moreover, the operation with the same said of what changed carbonyl into the oxime ether is shown. Specifically, it is 2. - After reacting these and hydroxy amines to alkyl-1-[4-(alkylthio) phenyl]-2-morpholino Pronon -1 kind and a list, the oxime ether which etherified N-OH can be raised.

Sulfinate: An activity radical can be generated in reduction. A concrete target can raise aryl SURUFIN ** sodium etc.

[0105] (c) Compound:, for example, the compound group which has SH, PH, SiH, and GeH in intramolecular, which reacts with a radical and acts on a high activity radical as conversion or a chain transfer agent is used. These carry out hydrogen supply at the radical kind of low activity, and after they generate a radical or oxidize, they can generate a radical by carrying out deprotonate. Specifically, 2-mercaptobenzimidazole is raised.

[0106] For example, into JP,9-236913,A, as an additive aiming at the improvement in sensibility, many more concrete examples of these co-sensitizers are indicated, and can apply them also in this invention. These co-sensitizers are independent, or can be used together two or more sorts, and can be used. the compound 100 weight section in which the amount used has an ethylene nature partial saturation double bond -- receiving -- the 0.05 - 100 weight section -- desirable -- 1 - 80 weight section -- the range of 3 - 50 weight section is still more preferably suitable.

[0107] (E-2) In order to prevent the unnecessary thermal polymerization of the compound which has the ethylene nature partial saturation double bond in which a polymerization is possible in polymerization inhibitor and this invention during [other than the above fundamental component] during manufacture of a thermosensitive constituent, or preservation, it is desirable to add a small amount of thermal polymerization inhibitor. As a suitable thermal polymerization inhibitor, hydroquinone, p-methoxy phenol, G t-butyl-p-cresol, pyrogallol, t-butyl catechol, a benzoquinone, 4,4'-thiobis (3-methyl-6-t-butylphenol), 2,2'-methylene bis (4-methyl-6-t-butylphenol), the first cerium salt of an N-nitroso phenyl hydroxy amine, etc. are mentioned. The addition of a thermal polymerization inhibitor has about 0.01 % of the weight - about 5 desirable % of the weight to the weight of all constituents. Moreover, in order to prevent the polymerization inhibition by oxygen, when adding behenic acid, a higher-fatty-acid derivative like a behenic acid amide, etc. and considering as the original edition for the lithography versions if needed, you may make it unevenly distributed in the front face of the recording layer in process of desiccation after spreading to a base material etc. About 0.5 % of the weight - about 10% of the weight of all the constituents of the addition of a higher-fatty-acid derivative are desirable.

[0108] (E-3) Further, a coloring agent etc. may add a color or a pigment for the purpose of coloring of the recording layer, when using the thermosensitive constituent of this invention for the original edition for the lithography versions. Thereby, the visibility after platemaking as a printing version and so-called proof comparison nature called image density measurement machine fitness can be raised. As a coloring agent, since many colors produce the fall of the sensibility of a photopolymerization system recording layer, especially as a coloring agent, its use of a pigment is desirable. As an example, there are colors, such as pigments, such as phthalocyanine pigment, azo pigment, carbon black, and titanium oxide, ethyl violet, a crystal violet, an azo system color, an anthraquinone system color, and a cyanine system color. About 0.5 % of the weight - about 5% of the weight of all the constituents of the addition of a color and a pigment are desirable.

[0109] (E-4) When using the thermosensitive constituent of this invention for the original edition for the lithography versions, in order to improve the physical properties of a hardening coat, an inorganic bulking agent and an additive with a plasticizer, the affinitizing agent in which the ink impression nature on the front face of a recording layer is raised, and it deals well-known in addition to this may be added to other additive pans.

[0110] As a plasticizer, there are dioctyl phthalate, didodecyl phthalate, triethylene glycol dicaprylate,

dimethyl glycol phthalate, tricresyl phosphate, dioctyl adipate, dibutyl sebacate, a thoria cetyl glycerol, etc., and when a binder is used, it can add 10 or less % of the weight to the sum total weight of the compound and binder which have an ethylene nature partial saturation double bond.

[0111] Moreover, addition of UV initiator for strengthening the effectiveness of heating and exposure after the development aiming at the improvement in film on the strength (print durability) mentioned later, *****, etc. can also be performed. In addition, it is possible in preparing the additive for raising the improvement in adhesion with a recording layer and a base material, and the development removal nature of an unexposed recording layer, and an interlayer. For example, adhesion improves by addition and the under coat of the compound which has diazonium structure, and a substrate and the compounds which have a strong interaction comparatively, such as a HOSUHON compound, it is possible to raise print durability, on the other hand, by the addition and the under coat of a hydrophilic polymer like polyacrylic acid and a polysulfone acid, the development nature of the non-image section improves and improvement in dirt nature is attained.

[0112] In order to offer the lithography version, in case the thermosensitive constituent of this invention is applied on a base material, it melts to various organic solvents and use is presented. As a solvent used here, an acetone, a methyl ethyl ketone, a cyclohexane, Ethyl acetate, ethylene dichloride, a tetrahydrofuran, toluene, Ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, Ethylene glycol wood ether, propylene glycol monomethyl ether, The propylene glycol monoethyl ether, an acetylacetone, a cyclohexanone, Diacetone alcohol, ethylene glycol monomethyl ether acetate, Ethylene glycol ethyl ether acetate, ethylene glycol mono-isopropyl ether, Ethylene-glycol-monobutyl-ether acetate, 3-methoxy propanol, Methoxy methoxy ethanol, the diethylene-glycol monomethyl ether, Diethylene glycol monoethyl ether, diethylene-glycol wood ether, Diethylene-glycol diethylether, propylene-glycol-monomethyl-ether acetate, There are propylene glycol monoethyl ether acetate, 3-methoxy propyl acetate, N, and N-dimethylformamide, dimethyl sulfoxide, gamma-butyrolactone, methyl lactate, ethyl lactate, etc. these solvents are independent -- or it can be mixed and used. And 2 - 50 % of the weight is suitable for the concentration of the solid content in a spreading solution.

[0113] As for the coverage to the base material of said recording layer, it is desirable to choose suitably according to an application in consideration of the effect of the sensibility of a recording layer, development nature, reinforcement, print durability of the exposure film, etc. Print durability becomes less enough when there is too little coverage. In many [too], when sensibility falls and exposure takes time amount on the other hand, it is not desirable in order for a development to also take longer time amount. Generally the range of abbreviation 0.1g/m² - about 10 g/m² is suitable for the coverage in the lithography version original edition of this invention by the weight after desiccation. It is 0.5 - 5 g/m² more preferably.

[0114] (Protective layer) In the lithography version original edition of this invention, a protective layer can be prepared on the recording layer containing the compound of polymerization nature if needed. Although such the lithography version original edition is usually exposed in atmospheric air, a protective layer prevents mixing to the recording layer of low molecular weight compounds, such as oxygen which exists in the atmospheric air which checks the image formation reaction produced by exposure in a recording layer, and an alkali, and prevents inhibition of the image formation reaction by exposure in atmospheric air. Therefore, it is that the permeability of low molecular weight compounds, such as oxygen, is low, the property which such a protective layer is expected has the good permeability of the light used for exposure, and it is still more desirable that it excels in adhesion with a recording layer, and can remove easily at the development process after exposure.

[0115] Such a device about a protective layer is made conventionally, and is indicated in detail by United States patent No. 3,458,311 and JP,55-49729,A. If it considers as the ingredient which can be used for a protective layer, it is good to use the water soluble polymer compound excellent in crystallinity comparatively, and that water-soluble polymers, such as polyvinyl alcohol, a polyvinyl pyrrolidone, acid celluloses, gelatin, gum arabic, and polyacrylic acid, are known, and ** specifically uses polyvinyl alcohol as a principal component among these gives the best results in basic property, such as oxygen cutoff nature and development removal nature. As long as the polyvinyl

alcohol used for a protective layer contains the non-permuted vinyl alcohol unit for having required oxygen cutoff nature and water solubility, the part may be permuted by ester, the ether, and the acetal. Moreover, the part may have other copolymerization components similarly.

[0116] As an example of polyvinyl alcohol, it hydrolyzes 71 to 100%, and molecular weight can raise the thing of the range of 2400 from 300. Specifically PVA-105 by Kuraray Co., Ltd., PVA-110, PVA-117, PVA-117H, PVA-120, PVA-124, PVA-124H, PVA1CS, PVA-CST, PVA1HC, PVA-203, PVA-204, PVA-205, PVA-210, PVA-217, PVA-220, PVA-224, PVA-217EE, PVA-217E, PVA-220E, PVA-224E, PVA-405, PVA-420, PVA-613, and L-8 grade are mentioned.

[0117] The component (selection of PVA, use of an additive) of a protective layer, coverage, etc. are chosen in consideration of others and fogging nature, and adhesion and damage resistance. [nature / oxygen cutoff nature and / development removal] Oxygen cutoff nature becomes high and is so advantageous that thickness is so so thick that the rate of hydrolysis of PVA generally used is high (that the non-permuted vinyl alcohol unit content in a protective layer is high) in respect of sensibility. However, if oxygen cutoff nature is raised extremely, the problem of being as **** of unnecessary fogging and a streak arising at the time of image exposure **** [, and] will be produced. [that an unnecessary polymerization reaction arises at the time of - raw preservation at the time of manufacture] Moreover, adhesion with the image section and damage resistance are also very important on the handling of a version. That is, if the laminating of the layer of the hydrophilic property which consists of a water-soluble polymer is carried out to the polymerization layer of fresh oil nature, it will be easy to generate the film exfoliation by the lack of adhesive strength, and an exfoliation part will cause the defect of poor film hardening by polymerization inhibition of oxygen.

[0118] On the other hand, various proposals are made that the adhesive property between two-layer [these] should be *(ed). For example, it is indicated by United States patent 292nd, No. 501, United States patent 44th, and No. 563 by mixing an acrylic emulsion or a water-insoluble nature vinyl-pyrrolidone-vinyl acetate copolymer 20 to 60% of the weight, and carrying out a laminating on a polymerization layer into the hydrophilic polymer which mainly consists of polyvinyl alcohol, that sufficient adhesive property is acquired. To the protective layer in this invention, each of these well-known techniques is applicable. The method of application of such a protective layer is indicated in detail by U.S. Pat. No. 3,458,311 and JP,55-49729,A, for example.

[0119] Furthermore, other functions can also be given to a protective layer. For example, safe light fitness can be further raised by addition of coloring agents (water soluble dye etc.) which is excellent in the permeability of the light (for example, if it is infrared laser wavelength of 760-1200nm) used for exposure, and may absorb the light of the wavelength without regards to exposure efficiently, without causing a sensibility fall.

[0120] (Resin interlayer) In the lithography version original edition of this invention, the resin interlayer who consists of an alkali fusibility macromolecule can be prepared between the recording layers and base materials containing the compound of B-1 polymerization nature if needed. By the recording layer containing the compound of the photopolymerization nature which is the infrared induction layer to which the solubility to an alkali developer falls by exposure being prepared in an exposure side or its near, while the sensibility to infrared laser is good, this resin interlayer exists between a base material and the recording layer of this infrared sensitivity, and since the heat generated by exposure of infrared laser is not spread in a base material but is used efficiently, high-sensitivity-ization can be attained by functioning as a thermal break. Moreover, in order that the sensitization layer which became non-permeability to the alkali developer may function as this resin interlayer's protective layer in the exposure section While development stability becomes good, it is thought that the image excellent in discrimination is formed and stability with time is also secured, and it sets in the unexposed section. Promptly, a non-hardened binder component dissolves in a developer and distributes. Further Since it is what this resin interlayer that adjoins and exists in a base material becomes from an alkali fusibility macromolecule, the solubility over a developer is good. For example, even when the developer with which activity fell is used, in order to dissolve promptly, without a residual membrane etc. occurring, it is thought that it excels in development nature.

[0121] (Base material) As a base material used for the lithography version original edition of this invention If it is a tabular object stable in dimension, there will be especially no limit. For example, paper, plastics The paper (which for example, polyethylene, polypropylene, polystyrene, etc. laminated), A metal plate, plastic film (for example, aluminum, zinc, copper, etc.) for example, diacetyl cellulose, a cellulose triacetate, and cellulose propionate -- a butanoic acid cellulose, a cellulose acetate butyrate, a cellulose nitrate, polyethylene terephthalate, polyethylene, polystyrene, polypropylene, a polycarbonate, a polyvinyl acetal, etc. -- etc. -- it is mentioned. The paper in which these may be the sheets of single components, such as a resin film and a metal plate, or may be the layered products of two or more ingredients, for example, the metal like the above was laminated or vapor-deposited, plastic film, the laminating sheet of a plastic film comrade of a different kind, etc. are contained.

[0122] As said base material, polyester film or an aluminum plate is desirable, also in it, dimensional stability is good and especially a comparatively cheap aluminum plate has it. [desirable] A suitable aluminum plate may be an alloy plate which uses a pure aluminium plate and aluminum as a principal component, and contains the different element of a minute amount, and the plastic film with which aluminum was laminated or vapor-deposited further is sufficient as it. There are silicon, iron, manganese, copper, magnesium, chromium, zinc, a bismuth, nickel, titanium, etc. in the different element contained in an aluminium alloy. The content of the different element in an alloy is at most 10 or less % of the weight. Although especially suitable aluminum is pure aluminium in this invention, since manufacture on a refinement technique is difficult for completely pure aluminum, a different element may be contained slightly. Thus, the presentation is not specified and the aluminum plate of the material of well-known official business can be conventionally used for the aluminum plate applied to this invention suitably. The thickness of said aluminum plate is 0.2-0.3mm especially preferably 0.15-0.4mm preferably about about 0.1-0.6mm.

[0123] It precedes carrying out surface roughening of the aluminum plate, and cleaning processing by the surfactant, the organic solvent, or the alkali water solution in order for a request to remove surface rolling oil is performed. Although the surface roughening process of the front face of an aluminum plate is performed by various approaches, it is performed by the approach of carrying out surface roughening mechanically, for example, the approach of carrying out dissolution surface roughening of the front face electrochemically, and the approach of carrying out selective dissolution of the front face chemically. As the mechanical approach, well-known approaches, such as the ball grinding method, a brushing method, the blasting grinding method, and buffing, can be used. Moreover, there is the approach of performing according to an alternating current or a direct current in a hydrochloric acid or the nitric-acid electrolytic solution as an electrochemical surface roughening method. Moreover, the approach which combined both as indicated by JP,54-63902,A can also be used. Thus, by request, through alkali etching processing and neutralization processing, the aluminum plate by which surface roughening was carried out can perform anodizing, in order to raise surface water retention and abrasion resistance. As an electrolyte used for anodizing of an aluminum plate, use of the various electrolytes which form a porosity oxide film is possible, and, generally a sulfuric acid, a phosphoric acid, oxalic acid, chromic acids, or those mixed acids are used. The concentration of those electrolytes is suitably decided according to an electrolytic class.

[0124] Since the processing conditions of anodic oxidation change variously with the electrolyte to be used, it cannot generally specify, but generally, if electrolytic concentration is 5-70 degrees C, current density 5 - 60 A/dm², electrical potential differences 1-100V, and the range for 10 seconds - electrolysis time amount 5 minutes, it is suitable for a 1 - 80-% of the weight solution, and solution temperature. The amount of an anodic oxide film is 1.0g/m². Although the above is suitable, it is 2.0 - 6.0 g/m² more preferably. It is the range. Anodized coating is 1.0 g/m². Print durability is inadequate in it being the following, or it becomes easy to produce the so-called "blemish dirt" with which a blemish becomes easy to stick to the non-image section of the lithography version with, and ink adheres to the part of a blemish at the time of printing. In addition, such anodizing is 0.01 - 3 g/m² also to a rear face by the circumference of the flesh side of line of electric force, although given to the field used for printing of the base material of the monotonous printing version. It is common that anodized coating is formed.

[0125] Hydrophilization processing of a support surface is performed after the above-mentioned anodizing, and the approach known conventionally is used. alkali-metal silicate (for example, specific silicate water solution) which is indicated by U.S. Pat. No. 2,714,066, 3,181,461, No. 3,280,734, and the No. 3,902,734 official report as such hydrophilization processing -- there is law. In this approach, immersion processing of the base material is carried out in a specific silicate water solution, or electrolysis processing is carried out. The approach of processing by polyvinyl phosphonic acid which is indicated by the fluoride zirconic acid potassium currently otherwise indicated by JP,36-22063,B and U.S. Pat. No. 3,276,868, 4,153,461, and the 4,689,272 official report etc. is used. In these, especially desirable hydrophilization processing is silicate processing in this invention. Silicate processing is explained below.

[0126] In the anodic oxide film of the aluminum plate which performed processing like ****, 0.1 to 30% of the weight, alkali-metal silicate is 0.5 - 10 % of the weight preferably, and is immersed in the water solution whose pH in 25 degrees C is 10-13 for 0.5 to 120 seconds at 15-80 degrees C. If pH of an alkali-metal silicate water solution is lower than 10, liquid will be gelled, and an oxide film will be dissolved if higher than 13.0. As alkali-metal silicate used for this invention, a specific silicate, a potassium silicate, a silicic acid lithium, etc. are used. As a hydroxide used in order to make high pH of an alkali-metal silicate water solution, there are a sodium hydroxide, a potassium hydroxide, a lithium hydroxide, etc. in addition, the above-mentioned processing liquid -- the [an alkaline-earth-metal salt or] -- an IVB group metal salt may be blended. As an alkaline earth metal salt, water-soluble salts, such as a calcium nitrate, a strontium nitrate, a magnesium nitrate, a nitrate like a barium nitrate, and a sulfate, a hydrochloride, phosphate, acetate, an oxalate, a borate, are mentioned. the -- a titanium tetrachloride, a titanium trichloride, a titanium fluoride potassium, a titanous oxalate potassium, sulfuric-acid titanium, 4 titanium iodide, a chlorination zirconium dioxide, a zirconium dioxide, zirconium oxychloride, a zirconium tetrachloride, etc. can be mentioned as an IVB group metal salt. the [an alkaline-earth-metal salt or] -- an IVB group metal salt is independent -- or it can be used, combining two or more. The desirable range of these metal salts is 0.01 - 10 % of the weight, and the still more desirable range is 0.05 - 5.0 % of the weight. By silicate processing, since the hydrophilic property on an aluminum plate front face is improved further, in case it is printing, ink stops being able to adhere to the non-image section easily, and the dirt engine performance improves.

[0127] A back coat is established in the rear face of a base material if needed. The enveloping layer which consists organic [an organic high molecular compound given in JP,5-45885,A and given in JP,6-35174,A] or inorganic metallic compounds of hydrolysis and a metallic oxide which is made to carry out a polycondensation and is obtained as this back coat is used preferably. Si₄ among these enveloping layers (OCH₃), Si (OC two H₅)₄, Si (OC three H₇)₄, and Si (OC four H₉)₄ etc. -- the enveloping layer of a metallic oxide which the alkoxy compound of silicon has, and is easy to come to hand, and receives is especially excellent in development-proof nature, and desirable. [cheap]

[0128] (Exposure) The lithography version original edition of this invention can be created as mentioned above. Image exposure of this lithography version original edition is carried out by the solid state laser and semiconductor laser which emit 1200nm infrared radiation from the wavelength of 760nm. In this invention, although a development may be immediately performed after laser radiation, you may heat-treat between a laser radiation process and a development process. As for the conditions of heat-treatment, it is desirable to carry out for [10 seconds -] 5 minutes within the limits of 80 degrees C - 150 degrees C. By this heat-treatment, laser energy required for record can be decreased at the time of laser radiation.

[0129] (Development) After the lithography version original edition of this invention carries out image exposure with infrared laser, it is usually preferably developed in water or an alkaline water solution. In this invention, although a development may be immediately performed after laser radiation, heating down stream processing can also be prepared between a laser radiation process and a development process. The range of heat-treatment conditions is 80 degrees C - 150 degrees C, and it is desirable to carry out for [10 seconds -] 5 minutes. By this heat-treatment, laser energy required for record can be decreased at the time of laser radiation. As a developer, an alkaline water solution is desirable and it is

still more desirable as a desirable pH field for the range of pH 10.5-12.5 to be mentioned, and to carry out a development with the alkaline water solution of the range of pH 10.0-12.5. When a with a pH of less than 10.5 thing is used as an alkaline water solution, the inclination dirt becomes easy to produce in the non-image section, and when a development is carried out with the water solution exceeding pH 12.5, there is a possibility that the reinforcement of the image section may fall.

[0130] As a developer, when using an alkaline water solution, as the developer and replenisher of an image recording ingredient of this invention, a well-known alkali water solution can be used conventionally. For example, inorganic alkali salt, such as a sodium silicate, this potassium, the 3rd sodium phosphate, this potassium, this ammonium, the 2nd sodium phosphate, this potassium, this ammonium, a sodium carbonate, this potassium, this ammonium, a sodium hydrogencarbonate, this potassium, this ammonium, way acid sodium, this potassium, this ammonium, a sodium hydroxide, this ammonium, this potassium, and this lithium, is mentioned. Moreover, organic alkali chemicals, such as monomethylamine, dimethylamine, a trimethylamine, a monoethyl amine, diethylamine, triethylamine, mono-isopropylamine, diisopropylamine, a triisopropyl amine, n butylamine, monoethanolamine, diethanolamine, triethanolamine, monoisopropanolamine, diisopropanolamine, ethyleneimine, ethylenediamine, and a pyridine, are also used. These alkali chemicals are used combining independent or two sorts or more.

[0131] Furthermore, it is known that a lot of lithography version original editions can be processed, without exchanging the developer in a developing tank for a long time by adding a water solution with alkali reinforcement higher than the same thing or same developer as a developer (replenisher) to a developer, in developing negatives using an auto-processor. Also in this invention, this supplement method is applied preferably.

[0132] Various surfactants, organic solvents, etc. can be added if needed in order to raise the parent ink nature of promotion of development nature, control, distribution of development dregs, and the printing version image section to a developer and a replenisher. It is desirable to add a surfactant one to 20% of the weight into a developer, and it is 3 - 10% of the weight of the range more preferably. The development disposition top effectiveness is not fully acquired as the addition of a surfactant is less than 1 % of the weight, but it will become easy to come out of the evil of reinforcement, such as the abrasion resistance of an image, falling if it adds exceeding 20 % of the weight. As a desirable surface active agent, an anion system, a cation system, the Nonion system, and an amphoteric surface active agent are mentioned. Specifically For example, the sodium salt of lauryl alcohol sulfate, The ammonium salt of lauryl alcohol sulfate, the sodium salt of octyl alcohol sulfate, For example, sodium salt of an isopropyl naphthalene sulfonic acid, sodium salt of an isobutyl naphthalene sulfonic acid, The sodium salt of polyoxy-ethylene-glycol mono-naphthyl ethyl-sulfuric-acid ester, Alkylaryl sulfonates, such as sodium salt of DODENRU benzenesulfonic acid, and sodium salt of a meta-nitrobenzene sulfonic acid, The higher-alcohol sulfates of the carbon numbers 8-22, such as the 2nd sodium alkyl sulfate Fatty alcohol phosphate, such as sodium salt of cetyl alcohol phosphoric ester For example, the sulfonates of alkylamide, such as $C_{17}H_{33}CON(CH_3)CH_2CH_2SO_3Na$ For example, the sulfonates of dibasicity aliphatic series ester, such as sodium sulfo succinic-acid dioctyl ester and sodium sulfo succinic-acid dihexyl ester For example, ammonium salt, such as lauryl trimethylammonium chloride and a lauryl trimethylammonium methosulfate For example, amine salts, such as stearamide ethyl diethylamine acetate, For example, polyhydric alcohol, such as fatty acid monoester of glycerol, and fatty acid monoester of pentaerythritol For example, polyethylene-glycol ethyl, such as polyethylene-glycol mono-naphthyl ethyl and polyethylene-glycol monochrome (Noel phenol) ethyl, is contained.

[0133] As a desirable organic solvent, about 10 or less % of the weight of a thing is mentioned for the solubility to water, and the solubility to water is chosen from 5 or less % of the weight of a thing still more preferably. For example, 1-phenyl ethanol, 2-phenyl ethanol, 3-phenylpropanol, 1, 4-phenyl butanol, 2, and 2-phenyl butanol, 1, 2-phenoxyethanol, 2-benzyloxy ethanol, o-methoxybenzyl alcohol, m-methoxybenzyl alcohol, p-methoxybenzyl alcohol, benzyl alcohol, a cyclohexanol, 2-methyl cyclohexanol, 4-methyl cyclohexanol, 3-methyl cyclohexanol, etc. can be mentioned. 1 - 5 % of the weight is suitable for the content of an organic solvent to the AUW of the developer at the time of use.

As for the amount of a surfactant, it is desirable to make it increase as the amount used has as close relation as the amount of the surfactant used and the amount of an organic solvent increases. This is in a condition with few amounts of a surfactant, and is because an organic solvent does not dissolve, therefore it becomes impossible to expect reservation of good development nature, when many amounts of an organic solvent are used.

[0134] Furthermore, a developer and a replenisher can also be made to contain a defoaming agent and an additive like a water softener if needed. As a water softener, for example Polyphosphates, such as $\text{Na}_2\text{P}_2\text{O}_7$, $\text{Na}_5\text{P}_3\text{O}_{10}$, $\text{Na}_3\text{P}_3\text{O}_9$, $\text{Na}_2\text{O}_4\text{P}(\text{NaO}_3\text{P})_2$, and Calgon (polymetaphosphate sodium), For example, ethylene-diamine-tetraacetic acid, its potassium salt, its sodium salt; Diethylenetriaminepentaacetic acid, The potassium salt, sodium salt; A triethylenetetramine hexa acetic acid, The potassium salt, its sodium salt; A hydroxyethyl ethylene DIAMINTORI acetic acid, The potassium salt, its sodium salt; Nitrilotriacetic acid, its potassium salt, The sodium salt; 1, a 2-diamino cyclohexane tetra-acetic acid, its potassium salt, The sodium salt, 1, a 3-diamino-2-propanol tetra-acetic acid, Others [polycarboxylic acid /, such as the potassium salt and its sodium salt / amino], 2-phosphono butane tricarboxylic acid - 1, 2, 4, potassium salt of those, The sodium salt; 2-phosphono butanone tricarboxylic acid - 2, 3, 4, potassium salt of those, The sodium salt; 1-phosphono ethane tricarboxylic acid - 1, 2, 2, potassium salt of those, The sodium salt; organic phosphonic acid, such as 1-hydroxy ethane -1, 1-diphosphonic acid, its potassium salt, its sodium salt; friend NOTORI (methylene phosphonic acid), its potassium salt, and its sodium salt, can be mentioned. Although the optimal amount of such a water softener changes according to the degree of hardness of hard water used, and its amount used, generally, into the developer at the time of use, 0.01 to 5% of the weight, it is made to contain in 0.01 - 0.5% of the weight of the range more preferably, and it deals in it.

[0135] Furthermore, since a developer gets fatigued according to throughput in developing this lithography version using an auto-processor, a throughput may be recovered using a replenisher or a fresh developer. In this case, it is desirable to supply with the approach indicated by U.S. Pat. No. 4,882,246.

[0136] As a developer containing such a surfactant, an organic solvent, a reducing agent, etc. For example, the benzyl alcohol indicated by JP,51-77401,A, Are indicated by the developer constituent which consists of an anionic surfactant, alkali chemicals, and water, and JP,53-44202,A. Benzyl alcohol, an anionic surfactant, and the developer constituent that consists of an aqueous solution containing a water-soluble sulfite, The developer constituent with which the solubility to water indicated by JP,55-155355,A contains the organic solvent which is 10 or less % of the weight in ordinary temperature, alkali chemicals, and water is mentioned, and it is suitably used also in this invention.

[0137] After treatment of the printing version by which the development was carried out using the developer and replenisher which were described above is carried out with the rinse containing rinsing water, a surface active agent, etc., and the desensitization liquid containing gum arabic or a starch derivative. As after treatment in the case of using it as the printing version original edition, the image recording ingredient of this invention can be used combining various these processings.

[0138] In recent years, in platemaking / printing industry, the auto-processor for the plates for printing is widely used for rationalization of a platemaking activity, and a standardization. This auto-processor sprays and carries out the development of each processing liquid pumped up with the pump from a spray nozzle, consisting of the development section and the after-treatment section generally, consisting of the equipment and each processing cistern which convey the plate for printing, and spray equipment, and conveying the printing version [finishing / exposure] horizontally. Moreover, how to make carry out immersion conveyance of the printing version original edition with a guide-among liquid roll etc. into the processing cistern with which processing liquid was filled, and process is also learned recently. It can process in such automatic processing, supplementing each processing liquid with a replenisher according to throughput, the operating time, etc. Moreover, electrical conductivity can be sensed by the sensor and can also be filled up automatically. Moreover, the so-called disposable mode of processing substantially processed with intact processing liquid is also applicable.

[0139] Burning processing is performed to consider as the lithography version of much more high print-

durability, although presswork can be presented with it after the lithography version obtained as mentioned above applies desensitization gum by request. When carrying out the burning of the lithography version, it is desirable to process with counter etching liquid which is indicated by each official report of JP,61-2518,B, 55-28062, JP,62-31859,A, and 61-159655 in front of burning. The approach of immersing for it and applying the printing version as the approach into the bat which applied on the lithography version or filled counter etching liquid with sponge and the absorbent cotton into which this counter etching liquid was made to soak, spreading by the automatic coating machine, etc. are applied. Moreover, making it a squeegee, after applying, and making the coverage into homogeneity with a squeegee roller gives a more desirable result.

[0140] the processing to which the lithography version by which burning processing was carried out is suitably carried out from the former, such as rinsing and gum length, if needed -- ***** -- although things are made, when the counter etching liquid containing a water soluble polymer compound etc. is used, the so-called desensitization processing of gum length etc. can be omitted. the lithography version obtained by such processing is covered over the offset press etc. -- having -- many -- it is used for printing of several sheets.

[0141]

[Example] Hereafter, although the example of this invention is explained, this invention is not limited to these examples at all.

[0142] (Examples 1-10)

After washing the aluminum version (quality of the material 1050) with a [production of substrate] thickness of 0.3mm by the trichloroethylene and degreasing, using a nylon brush and the PAMISU-water suspension of 400 meshes, the graining front face was etched, it was immersed in the nitric acid for 20 seconds 20 more% after rinsing, and this front face was rinsed. The amounts of etching on the front face of graining at this time were about 3g/m². Next, after preparing the direct-current electrode oxide skin of 3 g/m² by current density 15 A/dm², having used the sulfuric acid as the electrolytic solution for this plate 7%, it rinsed, and it dried and the substrate [A] was created. With the 2 % of the weight water solution of specific silicates, the substrate [A] was processed for 15 seconds, was rinsed at 25 degrees C, and the substrate [B] was created.

[0143] [an interlayer's formation] -- the procedure of the following next -- SG -- the liquefied constituent (sol liquid) of law was adjusted.

<A sol liquid presentation> and a methanol 130g and water 20 g.85-% of the weight phosphoric acid 16g and tetra-ethoxy silane 50g and 3-methacryloxy propyl trimethoxysilane Each compound of 60g above was mixed and agitated. Generation of heat was accepted in about 5 minutes. After making it react for 60 minutes, sol liquid was obtained by moving contents to another container and adding methanol 3000g. Diluted this sol liquid with a methanol / ethylene glycol =9 / 1 (weight ratio), on the substrate [A] produced as mentioned above, applied so that the amount of Si on a substrate might be set to 3mg/m², and it was made to dry for 1 minute at 100 degrees C, and the substrate [C] was obtained.

[0144] [formation of the lithography version original edition] -- either the substrate [A] created as mentioned above thru/or the substrate [C] were used as the base material, the sensitization layer coating liquid of the following presentation was applied to the front face, it dried at 115 degrees C for 1 minute, the sensitization layer of 1.4 g/m² was formed, and the lithography version original edition of examples 1-10 was obtained. The compound and C light-and-heat conversion agent which have the partial saturation radical of the substrate to be used, A radical generating agent (it is indicated as a polymerization initiator all over Table 1), and B-1 polymerization nature, and the (D) binder are as being shown in the following table 1.

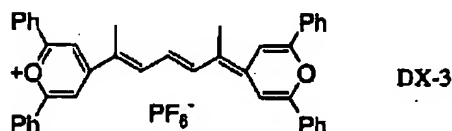
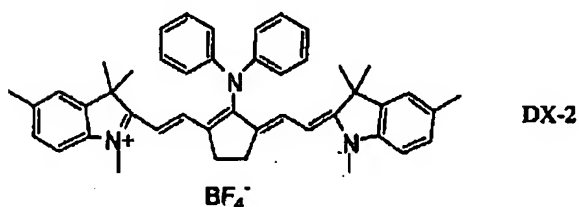
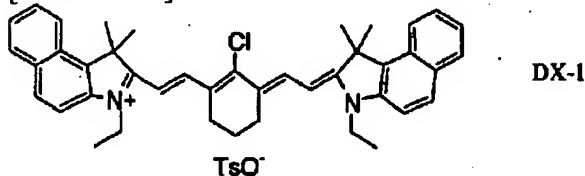
[0145]

(Sensitization layer coating liquid)

**A) A radical generating agent (compound given in Table 1) A 0.15 g-B-1 polymerization nature compound (compound given in Table 1) A 1.5 g-D binder (compound given in Table 1) A 2.0 g-C light-and-heat conversion agent (compound given in Table 1) 0.1g and a fluorine system nonionic surface active agent (F-177 ps of megger fucks) The Dainippon Ink & Chemicals, Inc. make The opposite anion

of 0.02g and the Victoria pure blue BOH 1-naphthalene 0.04g of colors, methyl ethyl ketone made into the sulfonic-acid anion 10g and methanol 7g and 2-methoxy-1-propanol 10g [0146]

[Formula 26]



[0147]

[Table 1]

	基板	重合開始剤	光熱変換剤	重合性化合物	イオン	現像液	感度 (mJ/cm ²)		感度 (mJ/cm ²)
実施例 1	A	SA-19	DX-2	M-1	B-1	D-1	80	実施例 1 1	65
実施例 2	B	SA-1	DX-1	M-2	B-2	DN-3C	90	実施例 1 2	75
実施例 3	C	SA-18	DX-3	M-2	B-1	D-1	95	実施例 1 3	80
実施例 4	A	SC-1	DX-2	M-1	B-1	DP-4	85	実施例 1 4	70
実施例 5	B	SE-3	DX-1	M-2	B-3	DP-4	90	実施例 1 5	75
実施例 6	C	SH-1	DX-1	M-2	B-1	DP-4	90	実施例 1 6	75
実施例 7	A	IG-10	DX-2	M-1	B-1	DN-3C	80	実施例 1 7	65
実施例 8	B	IA-1	DX-1	M-1	B-2	D-1	85	実施例 1 8	70
実施例 9	C	ID-4	DX-3	M-2	B-2	DP-4	90	実施例 1 9	75
実施例 1 0	B	IF-4	DX-1	M-2	B-2	DN-3C	90	実施例 2 0	70
比較例 1	A	HS	DX-1	M-2	B-2	DN-3C	110	比較例 4	95
比較例 2	B	HI	DX-3	M-2	B-2	DP-4	105	比較例 5	90

[0148] (Polymerization nature compound in Table 1)

(M-1)

Pentaerythritol tetraacrylate (M-2)

Glycerol dimethacrylate hexamethylene di-isocyanate urethane prepolymer [0149] (Binder in Table 1)

(B-1)

Allyl compound methacrylate / methacrylic acid / N-isopropyl amide copolymer (copolymerization mole ratio: 67/13/20)

Acid-number (it surveys with NaOH titration) 1.15 meq/g polymerization average molecular weight 130,000 (B-2)

Allyl compound methacrylate / methacrylic-acid copolymer (copolymerization mole ratio: 83/17)

Acid-number (it surveys with NaOH titration) 1.55 meq/g polymerization average-molecular-weight 125,000 (B-3)

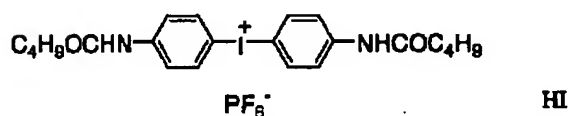
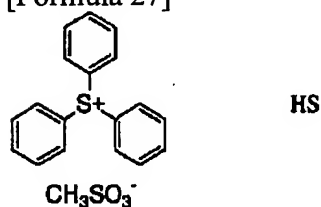
Polyurethane resin (a) 4, the 4'-(diphenylmethane diisocyanate b) (hexamethylene di-isocyanate c) polypropylene glycol (weight average molecular weight: 1000) which are the following diisocyanate and the condensate of diol

(d) 2 and 2-screw (hydroxymethyl) propionic acid ((a)/(b)/(c)/(d) copolymerization mole ratio: 40/10/15/35)

Acid-number (it surveys with NaOH titration) 1.05 meq/g polymerization average-molecular-weight 45,000 [0150] It replaces with the radical generating agent (polymerization initiator) expressed with A general formula (I) in said sensitization layer coating liquid on a substrate [A] and a substrate [B] for a comparison. (Examples 1 and 2 of a comparison) The sensitization layer was formed using the sensitization layer coating liquid of the presentation which the onium salt (polymerization initiator) (HS, HI) expressed with the following type which does not have sulfinic-acid structure as a counter anion was added, and also is shown in Table 1, and the original edition for the lithography versions was obtained (examples 1 and 2 of a comparison).

[0151]

[Formula 27]



[0152] The original edition for the lithography versions [development [exposure and]] Obtained The output of 500mW, the wavelength of 830nm, After exposing by 5m/second in horizontal-scanning rate using semiconductor laser with a beam diameter of 17 micrometers (1/e2), Negatives were developed using the auto-processor (Fuji Photo Film make-S processor 900VR) which taught a DNby Fuji Film company3C developer or DP-4 developer, and rinse FR-3 (1:7), and the following evaluations were performed. In addition, whether the development is faced and the developer of a gap was used wrote together to said table 1.

[0153] The [evaluation of sensibility] lithography version original edition was exposed with the semiconductor laser which emits infrared radiation with a wavelength of about 830-850nm. after exposure, developer DN[by Fuji Photo Film Co., Ltd.]-3C (it dilutes with the ratio of 1:2 with water), or the Fuji Photo Film Co., Ltd. make -- it developed negatives and rinsed by developer DP-4 (it dilutes with the ratio of 1:8 with water). The amount of energy required for record was computed based on the line breadth, the loss in a laser output and optical system, and scan speed of the image obtained at these times. It expresses that it is high sensitivity, so that a numeric value is small. These evaluation results are written together to Table 1.

[0154] The result of Table 1 shows that the original edition for the lithography versions of this invention is high sensitivity. On the other hand, it turned out that the lithography version original edition of the examples 1 and 2 of a comparison using a well-known radical polymerization initiator is mutually compared with the examples 2 and 9 acquired on the same conditions except [all] a polymerization initiator, and sensibility is inferior in it.

[0155] (Examples 11-20, examples 3 and 4 of a comparison) the recording layer top of the lithography version original edition obtained in said examples 1-10 and the examples 1 and 2 of a comparison --

polyvinyl alcohol (saponification whenever: -- 98-mol % --) Polymerization degree: It applied so that the coverage after drying the 3-% of the weight water solution of 550 might be set to 2g/m², and the lithography version original edition which dried for 2 minutes at 100 degrees C, and prepared the protective layer on the recording layer was obtained, and it considered as examples 11-20 and the examples 3 and 4 of a comparison, respectively. The obtained lithography version original edition was exposed and developed on the same conditions as the above-mentioned examples 1-10 and the examples 1 and 2 of a comparison, the lithography version was engraved, and sensibility was evaluated similarly. A result is written together to the above-mentioned table 1.

[0156] Although the inclination more nearly same than the result of Table 1 as the examples 1-10 and the examples 1 and 2 of a comparison which do not have a protective layer when a protective layer is prepared on a sensitization layer was seen, the lithography version original edition of this invention is excellent in sensibility and the inclination for the engine performance to improve by having prepared the protective layer was seen. The lithography version original edition of the examples 3 and 4 of a comparison using the onium salt which does not have sulfinic-acid structure as a polymerization initiator was compared with the example, and the gap was also inferior to sensibility in it.

[0157] (Example 21)

It applied with the wire bar so that the coverage after drying the coating liquid for the following resin interlayer formation might become the [formation of resin interlayer] aforementioned substrate [A] with 0.6 g/m², and it dried for 45 seconds at 120 degrees C with the warm air type dryer, and the resin interlayer was formed. Furthermore, the following sensitization layer coating liquid 2 was applied with the wire bar so that the coverage which doubled the interlayer and the sensitization layer might serve as 1.3 g/m², it dried for 50 seconds at 120 degrees C with the warm air type dryer, the sensitization layer was formed on the resin interlayer, and the lithography version original edition of an example 21 was obtained. Moreover, on this sensitization layer, it applied so that the coverage after drying the 3-% of the weight water solution of polyvinyl alcohol (whenever [saponification]: 98-mol %, polymerization-degree:550) might serve as 2 g/m² further, and it dried for 1 minute at 100 degrees C, the protective layer was prepared on the sensitization layer, and the lithography version original edition of an example 22 was obtained.

(Coating liquid for resin interlayers)

- Binder (BN-1) ... 2.0g N-(p-amino sulfonyl phenyl) methacrylamide Copolymer of butyl acrylate (35:65 mole ratios, weight average molecular weight 60,000)

- Fluorine system nonionic surface active agent ... 0.02g (megger fuck F-177P, Dainippon Ink & Chemicals, Inc. make)

- Naphthalene sulfonate of Victoria pure blue ... 0.04g - methyl ethyl ketone ... 10g - methanol ... 7g - gamma-butyrolactone ... 10g [0158]

(Coating liquid 2 for sensitization layers)

***B-1)** A polymerization nature compound [M-1] ... 1.5g -D binder [B-1] ... 2.0g -C light-and-heat conversion agent [DX-2] ... 0.1g -A radical generating agent [SA-20] ... 0.15g and fluorochemical surfactant ... 0.02g (megger fuck F-177P, Dainippon Ink & Chemicals, Inc. make)

- Naphthalene sulfonate of Victoria pure blue ... 0.04g - methyl ethyl ketone ... 20g - methanol ... 2g -2-methoxy-1-propanol ... 10g [0159] (Evaluation of sensibility) The lithography version original edition of the acquired example 21 was exposed with the semiconductor laser which emits infrared radiation with a wavelength of about 830-850nm immediately after preparation. It developed negatives and rinsed after exposure with the D-1 above-mentioned developer (it dilutes with the ratio of 1:5 with water). The amount of energy required for record was computed based on the line breadth, the loss in a laser output and optical system, and scan speed of the image obtained at these times. Consequently, the sensibility of an example 21 is 80 Jm/cm², and it turns out that it is high sensitivity. Also when the lithography version original edition of this invention took multistory structure including a resin interlayer, it turned out that high sensitivity can be attained.

[0160] (Example 22) As a base material, on the polyethylene terephthalate film (0.1mm in thickness), it applied so that the coverage after drying the following recording layer coating liquid might serve as 2.0

g/m², and the record ingredient of light yellow transparency was obtained.

(Recording layer coating liquid)

****B)** An oxidization developed color (leuco crystal violet) A 0.2 g-D binder (polymethylmethacrylate) A 2.7 g-A radical generating agent (SA-1) 0.3g and a methyl ethyl ketone 10g and methanol 8g and 2-methoxy-1-propanol 8g [0161] This record ingredient was heated in 200-degree C oven, and the recording layer for 15 seconds and on a base material was made to color. The recording layer was colored in vivid blue. As for the recording layer which consists of a thermosensitive constituent of this invention which contains from this the radical generating agent expressed with a general formula (I), leuco coloring matter is presumed to carry out oxidation coloring according to generating of a radical. [0162]

[Effect of the Invention] An irreversible change [high sensitivity physical properties / by heating] was possible for the thermosensitive constituent of this invention. Moreover, the negative-mold lithography version original edition using this thermosensitive constituent can be written in with infrared laser, and does so the effectiveness that record sensibility is high.

[Translation done.]